

THE ISOTHERMAL VAPOUR-LIQUID EQUILIBRIA  
IN THE SYSTEM  
ACETIC ACID-CHLOROFORM-WATER AT 25°C

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by  
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TO MY PARENTS

## ABSTRACT

The vapour-liquid equilibria of the two binary systems acetic acid-water and acetic acid-chloroform, and of the ternary system acetic acid-chloroform-water have been investigated. The data obtained have been corrected for dimerization of the acetic acid in the vapour phase. The results obtained on this basis show a positive deviation from Raoult's Law in the system acetic acid-water at 25°C. In the system acetic acid-chloroform Raoult's Law appears to be obeyed, showing pseudo-ideality on a dimerised basis. In the ternary system an increased deviation from Raoult's Law is observed, and this is mainly due to the fact that water and chloroform are only slightly miscible at 25°C. It seems that this treatment for dimerization of the acetic acid in the vapour phase is permissible and indeed highly desirable for a description of the thermodynamical behaviour of the vapour-liquid equilibria.

The densities have been determined for the system acetic acid-water and found to be in accordance with the data of previous authors.

The density data for the systems acetic acid-chloroform and acetic acid-chloroform-water have also been obtained at

25°C. From these data the excess molar volumes have been determined for the three systems. The excess molar volume in the system acetic acid-water is negative with a minimum value at a concentration of 50 mole percent acetic acid. The excess molar volume in the system acetic acid-chloroform is positive with a maximum at a concentration of 45 mole percent chloroform. In the ternary system there exists a region with a positive excess molar volume function and a region with a negative excess molar volume. A line has been obtained in the composition triangle showing the concentrations of the mixtures for which the excess molar volume is equal to zero. For these concentrations pseudo-ideality exists as far as the volume change on mixing is concerned.

The refractive indices were determined for all three systems. A calculation of the molar refractions in the systems acetic acid-water and acetic acid-chloroform shows that the "true molecular" volumes of acetic acid, water and chloroform are additive on mixing.

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## LIST OF SYMBOLS

|            |  |
|------------|--|
| $H^M$      | Enthalpy of mixing   |
| $S^M$      | Entropy of mixing  |
| $S^E$      | Excess entropy of mixing   |
| $G^M$      | Gibbs free energy of mixing  |
| $G^E$      | Excess Gibbs free energy of mixing   |
| $V^M$      | Volume of mixing   |
| $V^E$      | Excess volume of mixing  |
| $v^M$      | Partial molal volume of mixing   |
| $\mu^M$    | Thermodynamical potential of mixing  |
| P          | Pressure   |
| $x_i$      | Liquid mole fraction of component i  |
| $y_i$      | Vapour mole fraction of component i  |
| $\gamma_i$ | Activity coefficient of component i  |
| $n_D^t$    | Refractive index for Na-D line at $t^\circ\text{C}$                              |
| $d_4^{25}$ | Absolute density of liquid at $25^\circ\text{C}$                                 |
| L          | Functional relationship between vapour density, pressure and temperature (Gibbs) |

## INTRODUCTION

The system acetic acid-water-chloroform had already attracted attention as early as in 1891, when Wright, Thompson and Leon<sup>34</sup> carried out their investigations with respect to the binodal curve in this system at room temperature. Since then the system has been repeatedly studied, especially with respect to its application in solvent extraction.

Although many studies have been carried out on the practical application of this system hardly any attention has been devoted to describing the thermodynamics of this system or of its component binary systems. Some work has been done on the system water-acetic acid at 25°C, but the complete concentration range has never been covered. The purpose of the present study is to investigate some aspects of the thermodynamics of this system at 25°C. The usual thermodynamic data collected in isothermal studies are the mutual solubilities, which in this case have been studied thoroughly at room temperature only by previous workers, and also data on vapour pressures, volume changes, dielectric behaviour, heats of mixing and other data. In the present study the vapour-liquid equilibria and the volume changes have been considered in detail. The former allow of the description of the system in terms

of deviations from Raoult's Law or in terms of the Gibbs free energy function and the latter also indicate deviations from ideality.

A complication is introduced into systems containing acetic acid, due to the dimerization of the acetic acid in the vapour phase. In studies on systems with molecules that dimerise in the vapour phase special precautions have to be taken in calculations involving concentrations expressed in mole fractions. This was already pointed out by von Zawidzki<sup>9</sup> (1900). The results obtained in this research are treated for this dimerization and analysed in this way.

No theory of solutions, which gives an interpretation of data obtained in mixtures of dipoles, has as yet been developed. This is mainly because a statistical thermodynamical treatment of such mixtures becomes highly complicated. Also there is a great lack of experimental evidence which can support a developed theory. It is hoped that this study will be a small contribution to the experimental data and that in the not too distant future a theory may be developed by which the observed phenomena can be explained.



**THEORETICAL INTRODUCTION**

## A. GENERAL THEORY OF MIXTURES

### (1) PERFECT MIXTURES AND NON-PERFECT MIXTURES

In an account of the classical thermodynamics of mixtures Prigogine<sup>1</sup> (1957) provides definitions for the so called thermodynamic functions of mixing for non-electrolytes. It appears that all relations which are found in classical thermodynamics between extensive and intensive parameters hold for these functions of mixing.

The molar change in the Gibbs free energy due to mixing can be written in the case of binary mixtures as

$$G^M = G - x_1 G_1^{\circ} - x_2 G_2^{\circ} \quad (1)$$

Similarly

$$S^M = S - x_1 S_1^{\circ} - x_2 S_2^{\circ} \quad (2)$$

$$H^M = H - x_1 H_1^{\circ} - x_2 H_2^{\circ} \quad (3)$$

$$V^M = V - x_1 V_1^{\circ} - x_2 V_2^{\circ} \quad (4)$$

where  $H^M$  and  $V^M$  are the heat of mixing and the volume change on mixing respectively.

In a similar way partial molal quantities can be defined, for instance

$$\mu_i^M = \mu_i - \mu_i^{\circ} \quad (5)$$

$$N_i^M = N_i - N_i^{\circ} \quad (6)$$

All the above mentioned equations are equally valid in the case of ternary mixtures, in which case a third

term is added for the third component. For convenience sake, however, only the binary mixtures will be considered.

There is one type of mixture which is considered to be the ideal mixture or rather the perfect mixture. All mixtures showing a behaviour different from that of the perfect mixture are called imperfect mixtures.

A mixture is defined to be perfect if the Gibbs free energy of mixing takes the form

$$G^M = RT(x_1 \ln x_1 + x_2 \ln x_2) \quad (7)$$

If (7) is valid it follows necessarily that the heat of mixing and the volume change of mixing are equal to zero.

The entropy of mixing will be

$$S^M = - \frac{dG^M}{dT} = -R(x_1 \ln x_1 + x_2 \ln x_2) \quad (8)$$

and will not be zero. Therefore, in a perfect mixture all thermodynamic functions of mixing except those containing the entropy are equal to zero.

Most mixtures, however, show a behaviour that deviates from that of the perfect mixtures and hence also the laws of the perfect mixtures will not be obeyed. The deviation from "ideality" is often described by means of the deviations from Raoult's Law. A positive deviation from Raoult's Law is considered to be due to an increased

escaping tendency of the molecules in the mixture, and a negative deviation indicates a decrease in the escaping tendency. It seems that the use of the deviations from Raoult's Law for the characterization of the deviation from ideality is somewhat questionable, especially because, for instance, when there are large differences in the molar volumes of the components, the simple relations assumed in Raoult's Law have to be modified. This is discussed in detail by Guggenheim<sup>2</sup> (1937) and also by Fredenhagen<sup>3</sup> (1941). It appears therefore more advisable to define the deviations from the ideal behaviour by means of the thermodynamic functions of mixing.

G.N. Lewis<sup>4</sup> (1923) introduced the so called activity coefficients, which make it possible to express the deviations from the ideal thermodynamic functions formally. This leads to an expression for the molar free energy of mixing of the form

$$G^M = RT(x_1 \ln \gamma_1 x_1 + x_2 \ln \gamma_2 x_2) \quad (9)$$

where  $\gamma_i$  are the activity coefficients, which usually are determined from vapour pressures. In this case the functions  $V^M$  and  $H^M$  will not be equal to zero.

This leads to the introduction of a new type of thermodynamic function in the case of mixtures: the

the excess-functions. These functions have been introduced by Scatchard<sup>5</sup> (1931) and can be defined as follows: A thermodynamic excess function is defined by the difference between the thermodynamic function of mixing for an actual system and the thermodynamic function of mixing of a perfect system under the same conditions. From equation (9) would follow for example

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (10)$$

From the fact that the volume change on mixing and the heat of mixing are equal to zero for a perfect mixture, it follows that the volume changes and heats of mixing are by definition excess functions.

Generally  $G^E$  is determined by using the activity coefficients as obtained from vapour pressure data, while  $H^E$  is determined by the direct measurements of the heats of mixing. In this case there is the relation

$$TS^E = H^E - G^E \quad (11)$$

from which  $S^E$  can be calculated.

In many cases the activity coefficients are more complicated than those calculated from the vapour pressure data and in such a case usually the aid of statistical thermodynamics is involved to provide a means of calculating the excess-functions.

Kamke<sup>c</sup> and Kummerle<sup>6</sup> (1958) introduce a more general method for the classification of binary systems in regard to the thermodynamic excess functions  $TS^E$ ,  $H^E$  and  $G^E$ . These authors distinguish three major groups of binary mixtures, those for which  $G^E > 0$ ,  $G^E = 0$  and  $G^E < 0$ . For each group there are subdivisions depending on the sign of  $H$  and  $TS^E$ . A further subdivision is obtained due to the absence or occurrence of a point of inflexion in the concentration dependence curves of  $G^E$ ,  $H$  and  $TS^E$ . This classification may well be generalised to ternary systems, bearing in mind that such a system is composed of three binary systems.

## (2) SYSTEMS SHOWING MISCIBILITY GAPS

From the deviations from ideality two facts come to light. Either the liquids seem to have a great tendency to mix with each other, sometimes leading to compound formation, or there is just the reverse effect. In the latter case, where there is a tendency of the molecules of one species to remain in the environment of the molecules of their own kind rather than to mix freely with the molecules of the other species, there occurs as an ultimate effect a phase separation, where two liquid layers are present each containing more or less of the other species. When there is a phase separation one speaks of a miscibility gap.

In ternary systems there occur similar effects, creating one or more regions of immiscibility in the system.

The conditions under which these separations into

two or more liquid phases come into existence have been recently discussed by Haase<sup>7</sup> (1950) and Arich<sup>8</sup> (1955). Again in the explanations use is made of the excess functions, especially of the function  $G^E$ .

## B. VAPOUR PRESSURES AND ISOTHERMAL VAPOUR-LIQUID

### EQUILIBRIA

#### (1) VAPOUR PRESSURES AND PARTIAL VAPOUR PRESSURES

The vapour pressure of a liquid is defined as the pressure exerted by the vapour in equilibrium with the liquid at a certain temperature.

The same definition holds for mixtures of liquids, where the vapour pressure of the mixture is caused by both types of molecule that are present in the mixture. This leads to the concept of partial vapour pressures. The partial vapour pressure is defined as that part of the total vapour pressure which is due to the presence of one particular species of molecules. The magnitude of the partial vapour pressure depends on the concentration of the molecules of the species concerned in the vapour phase (Dalton's Law). The partial vapour pressure can be readily calculated from the mole fraction in the vapour phase of the species and the total vapour pressure using the relation

$$P_i = y_i P \quad (12)$$

In the case of perfect mixtures Raoult's Law is obeyed. This law is as follows: The escaping tendency of any chemical species is proportional to its mole fraction in the liquid phase. In a perfect solution the escaping tendency is measured exactly by the vapour pressures. Therefore

$$P_i = P_i^{\circ} x_i \quad (13)$$

For the total vapour pressure according to Dalton's Law there is the relation

$$P = (P_1^{\circ} x_1 + P_2^{\circ} x_2) \quad (14)$$

In the ideal case the  $P_i$  as defined in (12) and in (13) are equal. In the case of a non-perfect mixture this will not be so. From the difference between the actual partial vapour pressure calculated by means of equation (12) and the ideal vapour pressure as calculated from equation (13) it can be deduced whether a system shows a positive or negative deviation from Raoult's Law. The quotient of these two pressures leads to the concept of fugacity or activity. The term fugacity is used because this quotient indicates the escaping tendency of the molecules in the mixture.



(2) VAPOUR-LIQUID EQUILIBRIA

The dependence of the intensity variables in a multicomponent system is governed by the general Gibbs-Duhem equation

$$\sum_{i=1}^k x_i d\mu_i - VdP + SdT = 0 \quad (15)$$

von Zawidzki<sup>9</sup> (1900) emphasizes in his paper on the validity of the Gibbs-Duhem equation that when this equation is used in the form of (15), the mole fraction is determined by the molecular weight of the compounds concerned in the vapour phase. This follows from the fact that no surface work, but only work of dilution is being taken into account.

For an isothermal equilibrium therefore equation (15) becomes

$$\sum x_i d\mu_i - VdP = 0 \quad (16)$$

Kamke<sup>6</sup> (1958) shows how from this last equation the Gibbs-Duhem-Margules equation for a two component system is derived

$$\frac{d \ln P_1}{d \ln x_1} = \frac{d \ln P_2}{d \ln x_2} \quad (17)$$

von Zawidzki<sup>9</sup> undertook the task of studying various binary systems in regard to their pressure relationships and the Gibbs-Duhem-Margules equation. In this case he makes use of the exponential solutions, which were found for this differential equation by Margules<sup>10</sup> (1895), in a modified form

$$\begin{aligned} P_1 &= P x_1 \exp \left\{ \frac{\alpha_2}{2} x_2^2 + \frac{\alpha_3}{3} x_2^3 \right\} \\ P_2 &= P x_2 \exp \left\{ \frac{\beta_2}{2} x_1^2 + \frac{\beta_3}{3} x_1^3 \right\} \end{aligned} \quad (18)$$

where  $\beta_2 = \alpha_2 + \alpha_3$  and  $\beta_3 = -\alpha_3$

For the determination of the constants  $\alpha_2$  and  $\alpha_3$  one of the experimental partial pressure curves is applied, but if the results are not satisfactory this can be followed by further approximations. The results were in general satisfactory.

Kamke<sup>6</sup> makes use of the Gibbs-Duhem-Margules differential equation in the following form

$$x \frac{d \ln P_1}{dx} + (1 - x) \frac{d \ln P_2}{dx} = 0 \quad (19)$$

where  $x$  is the mole fraction of the component with the lower boiling point, in the liquid phase.

Since

$$\begin{aligned} P_1 &= yP \\ P_2 &= (1 - y)P \end{aligned} \quad (20)$$

where  $y$  is the mole fraction of the component with the lowest boiling point, in the vapour phase. This leads to the differential equation

$$\frac{1}{P} \frac{dP}{dx} = - \frac{x - y}{y(1 - y)} \frac{dy}{dx} \quad (21)$$

Kamke now writes  $f(y) = \frac{x - y}{y(1 - y)}$  and this is the equation of the equilibrium curve belonging to the total pressure curve. Use can be made of the plot of this function to obtain the  $P(x)$  curve from the  $y - x$  curve by stepwise integration. Lewis and Murphee<sup>11</sup> (1924) made use of this method. Scatchard and Raymond<sup>12</sup> (1938) used this function in order to obtain the total pressure in a similar way and to compare with the observed total pressures.

Kamke makes use of  $f(y)$  to obtain information on the course of the curve of the excess free energy for a binary system. He defines the molar free energy of mixing according to formula (10), so that

$$\frac{G^E}{RT} = x \ln \frac{Py}{P_1^0 x} + (1 - x) \ln \frac{P(1 - y)}{P_2^0 (1 - x)} \quad (22)$$

leading to

$$\frac{1}{RT} \frac{dG^E}{dx} = \ln \frac{P_2^0}{P_1^0} \cdot \frac{y(1-x)}{x(1-y)} = \ln \frac{P_2^0}{P_1^0} \alpha \quad (23)$$

where  $\alpha = \frac{y(1-x)}{x(1-y)}$  is the relative volatility, and

$$\begin{aligned} \text{also } \frac{1}{RT} \frac{d^2G^E}{dx^2} &= \frac{1}{y(1-y)} \left[ \frac{1}{1+(1-2y)f(y) + y(1-y) \frac{df(y)}{dy}} - \right. \\ &\quad \left. - \frac{1}{1+(1-2y)f(y) + y(1-y) \{-f^2(y)\}} \right] \quad (24) \end{aligned}$$

Generally one is interested in the sign of the curvature and the position of the maximum or minimum of the  $G^E$  curve.

If  $G^E$  may not show a point of inflexion of curvature in the interval  $0 \leq x \leq 1$  then it follows from (24) that

$$\frac{df(y)}{dy} > \begin{cases} > \\ < \end{cases} -f^2(y) \quad (25)$$

for all values of  $x$ .

The position of the maximum or minimum can be found with the aid of the relative volatility function and equation (23), because at the maximum or minimum,

$$\frac{dG^E}{dx} = 0.$$

(3) MIXTURES OF LIQUIDS WITH ABNORMAL VAPOUR DENSITIES

If one of the components of a binary liquid mixture in the vapour phase can exist in two modifications, for instance in monomeric and dimeric form, then also in this special case the Gibbs-Duhem-Margules equation remains valid. The mole fraction of the monomer-dimer component is calculated from the average molecular weight of that component in the vapour phase. von Zawidzki<sup>9</sup> proves this by means of a theoretical model.

Acetic acid is particularly suitable for studies on the validity of the Gibbs-Duhem-Margules equation, because it is possible to evaluate the vapour densities of acetic acid by a formula due to Gibbs<sup>13</sup> (1879) giving the relationship between the vapour density, the pressure and the temperature:

$$\Delta = 10 \log \frac{1000(\Delta-1)}{(2-\Delta)^2} = \frac{3520}{t+273} + 10 \log P - 8.349 \quad (26)$$

where  $\Delta = \frac{D}{D_1}$  and  $D_1 = 2.073$ , where  $D$  = vapour density.

Wrewsky et al<sup>14</sup> (1934) tested this formula on the system water-acetic acid at 42°C and 80°C and found that it reproduced their results over the complete concentration range.

Using formula (26) it is possible to calculate the

molecular weight of the acetic acid in the vapour phase by means of a method of successive approximation. In this method at first complete dimerization is assumed. From this the partial vapour pressure of acetic acid is calculated. From the formula the value of  $D$  is obtained, whence the molecular weight can be calculated. From this molecular weight again the partial vapour pressure is calculated. This procedure is repeated until no change in the average molecular weight is found. This enables us to construct the vapour pressure curves as a function of the concentration in mole fractions. The percentage dimerization can be calculated from the actual molecular weight of the acetic acid in the vapour phase, and from this again information on the partial pressures of the single and dimerised molecules can be obtained. A dimerization constant is now defined as follows

$$K = \frac{P(\text{dimer})}{P^2(\text{monomer})} \quad (27)$$

Lambert<sup>15</sup> (1953) points out that a plot of  $\log K$  against  $T^{-1}$  yields usually a linear plot, from which the heats and standard entropies of dimerization can be calculated. The values of  $\Delta s^\circ$  all lie between 20 and 27 cal/degree mole, the higher values being obtained for those molecules which show hydrogen bonding. However, for acetic acid Lambert finds from MacDougall's<sup>16</sup> (1936) data that  $\Delta H = -16 \text{ K cal/mole}$  and  $\Delta s^\circ = 54 \text{ cal/degree mole}$ . The entropy is two times the value of the expected entropy of dimerization. This is ascribed to the dimers being held together by two strong hydrogen bonds.

C. VOLUME RELATIONSHIPS IN MIXTURES OF NONELECTROLYTES

The change in molar volume on mixing of two liquids is defined as

$$V^M = V - x_1 V_1^{\circ} - x_2 V_2^{\circ}$$

This function is equal to the excess volume function  $V^E$ , because in a perfect mixture  $V^M$  is equal to zero.

For the partial molal volumes of mixing one can write

$$v_1^M = v_1^E = v_1 - v_1^{\circ}$$

The partial molal quantities were first introduced by G.N. Lewis with the aim of providing a mathematical way of reporting the volume contributions by the several components of the system under consideration. The partial molal volume is defined as the differential change with the mole fraction of one of the components of the total volume of a solution. In a paper on the significance of partial molal quantities in the theory of solutions Fredenhagen and Schulze<sup>17</sup> (1939) point out once more that partial molal quantities have no physical meaning. This is clearly shown in the well known system ethyl-alcohol-water, where negative partial molal volumes are obtained for the alcohol. This shows that there is such a change in the liquid structure that negative partial

molal volumes are caused. Hildebrand<sup>18</sup> (1939) also issued a warning with respect to the interpretation of partial molal quantities. The main significance of the partial molal quantities lies in the fact that they provide an excellent means for a formal description of the volume changes on mixing.

The partial molal volumes are calculated by means of the methods described by Lewis and Randall<sup>19</sup> (1961), making use of the apparent molal volumes and also of the  $V^E(x)$ -curve.

In an interesting paper Joerges and Nikuradse<sup>20</sup> (1950) discuss the excess molal volume in mixtures of nonelectrolytes. They discuss the sign of the excess function related to the degree of polarity of the substances. They also discuss the inter-relationship of the volume effect and the heat of mixing.

#### D. OPTICAL PROPERTIES OF MIXTURES OF NONELECTROLYTES

From the electromagnetic and magnetic theories of light H.A. Lorentz and L.V. Lorenz derived an expression giving the theoretical relationship between the refractive index and the density. This leads to the definition of the molar refraction.



$$R_M = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \quad (28)$$

the value of which depends only on the wave length of the light used for the measurement of the refractive index.

Rutgers<sup>21</sup> (1956) shows with a few examples that this function has approximately the same value in the liquid and in the gaseous state. Gladstone<sup>22</sup> (1947) points out that this property therefore may be regarded as a fundamental property of the compound. According to theoretical considerations, based on the assumption that molecules are perfectly conducting spheres the molar refraction for radiation at infinite wave length represents the actual volume of the molecules in one mole of substance. For radiation of a wave length of 5893Å (Sodium D line) this still is approximately true.

In the case of mixtures of two or more liquids the experimental value of the molar refraction is given by

$$R \text{ exp.} = \frac{n^2 - 1}{n^2 + 2} \frac{x_1 M_1 + x_2 M_2}{d} \quad (29)$$

In the ideal case this quantity should be equal to the sum of the contributions of the separate constituents

$$R \text{ ideal} = x_1 R_1 + x_2 R_2 \quad (30)$$

According to the Lorentz-Lorenz formula the molar

refraction for a pure substance is closely related to the problem of the polarity of a liquid. Rutgers<sup>21</sup> shows that for optical frequencies the following expression exists

$$\frac{n^2 - 1}{n^2 + 2} \frac{M}{d} = \frac{4 \pi N \alpha}{3} P_E \quad (31)$$

where  $\alpha$  is the polarisability of the molecules. This quantity is called the electron polarization, because this polarization represents that part of the total induced polarization, which is due to the distortion or deformation of the electronic shells in the molecule.

In modern theories on the dielectric properties the Lorentz-Lorenz formula is not frequently applied, but the refractive properties are often related in a fairly similar way both for pure liquids and liquid mixtures. A recent paper on the concentration dependence of the dipole moment in mixtures by Joerges and Nikuradse<sup>20</sup> reviews these modern theories.

REVIEW OF THE LITERATURE

(1) ACETIC ACID

The density of pure acetic acid as obtained from the International Critical Tables<sup>23</sup> (1930), abbreviated as I.C.T., is  $d_4^{25} = 1.0440 \text{ gms/cm}^3$ .

The vapour pressure of pure acetic acid was measured by numerous authors. From the data provided in the I.C.T. the value of 15.8 mm Hg is obtained for 25°C by means of graphical interpolation. McDougall<sup>16</sup> gives the value of 15.7 mm Hg.

(2) THE SYSTEM ACETIC ACID-WATER

This system has been intensively investigated both with regard to isobaric boiling point diagrams, and also with regard to isothermal vapour pressure curves.

The densities at 25°C are listed in the I.C.T.<sup>23</sup> with data up to 1915. Later data are available from Woodman<sup>24</sup> (1927) and Kohner and Gressmann<sup>25</sup> (1929), the latter of whom provides data on the refractive index at 25°C for the Helium D-line. Redlich and Nielsen<sup>26</sup> (1942) report on apparent molal volumes up to a concentration of 4 molal acetic acid using density data.

Isobaric studies on the system have been carried out by numerous authors, usually at atmospheric pressure (760 mm Hg). Arich and Tagliavini<sup>27</sup> give a list of

references on this subject.

Chalov and Aleksandrova<sup>29</sup> (1951) have investigated the isobaric diagrams at several pressures and from these they have deduced isotherms between 20°C and 80°C, but the extrapolation methods that were used for the data for the lower temperatures make the results doubtful. Wrewsky et al<sup>14</sup> have investigated the 42°C and 80°C isotherms using a method of isothermal distillation by means of air displacement, basically the same as will be described in this thesis. Their results show a positive deviation from Raoult's Law. Arich and Tagliavini<sup>27</sup> also investigated some of the isotherms at 69.7°C, 79.9°C and 89.9°C, and they come to similar conclusions. Fredenhagen and Liebster (1932) used the air displacement method to measure the partial pressures of acetic acid at 25°C up to 2.545 normal solutions. The results are interesting, but for the present study the main interests are in the pressure relationships over the complete range of concentration. Giacalone et al<sup>30</sup> (1942) report on the partial pressures of water at 34.45°C up to a concentration of 0.1529 mole fraction acetic acid.

Campbell and Kartzmark<sup>31</sup> (1950) report the relative viscosities at 25°C over the complete concentration range.

(3) THE SYSTEM WATER-CHLOROFORM

No data on the vapour pressures at 25°C are reported for this system.

This system shows a region of limited miscibility at 25°C and the limits are found to be 0.8 weight percent water and 99.4 weight percent water by Brancker et al<sup>32</sup> (1940). Wright, Thompson and Leon<sup>33</sup> (1891) found 0.99 and 99.16 weight percent water respectively. Reinders and de Minjer<sup>34</sup> (1947) mention a lower limit of .9 weight percent water at 25°C.

An investigation of the isobaric boiling point diagram at 760 mm Hg by Reinders and de Minjer<sup>34</sup> shows a minimum boiling point of 56.12°C at about 2.8 percent water. This might imply an azeotropic point at 25°C, but not necessarily so.

(4) THE SYSTEM WATER-CHLOROFORM-ACETIC ACID

This ternary system shows a miscibility gap. The binodal curve has been determined by Wright et al<sup>33</sup> and by Brancker et al<sup>32</sup>. The plait point can be determined using Alekseev's rule and a method developed by Tarasenkov<sup>35</sup> (1946) and is found to be:  $\text{CHCl}_3$  - 42.3%,  $\text{HA}_c$  - 42.4% and  $\text{H}_2\text{O}$ : 15.3%. This last method deserves an elaboration, because it will prove itself to be extremely

useful in ternary systems where miscibility gaps occur. Tarasenkov shows that if the tielines of the miscibility gap of a system, as represented in figure 1, are extended they will cut each other on the extension of the base A C in point K. Slight deviations are due to experimental errors in the determination of the tielines. A tangent from K to the binodal curve will produce the plait point P on this curve. From the figure it follows that the distribution of the co-dissolving constituent B in the two liquid layers is given by the equation

$$\frac{b_2}{b_1} = \frac{a_2 + k}{a_1 + k}$$

In the case where the co-dissolving constituent does not show dimerization this latter equation will represent the distribution coefficient. However, in the case of acetic acid-chloroform-water this will not be so. This is due to the larger dimerization of acetic acid in the chloroform layer. Hand<sup>37</sup> (1930) discusses the distribution of acetic acid monomers and dimers in the water and chloroform layers in the ternary system.

LEGEND TO FIGURE 1

The Method of Tarasenkov to Find The Plait Point  
in Ternary System

$a_1$  = concentration of A in 1

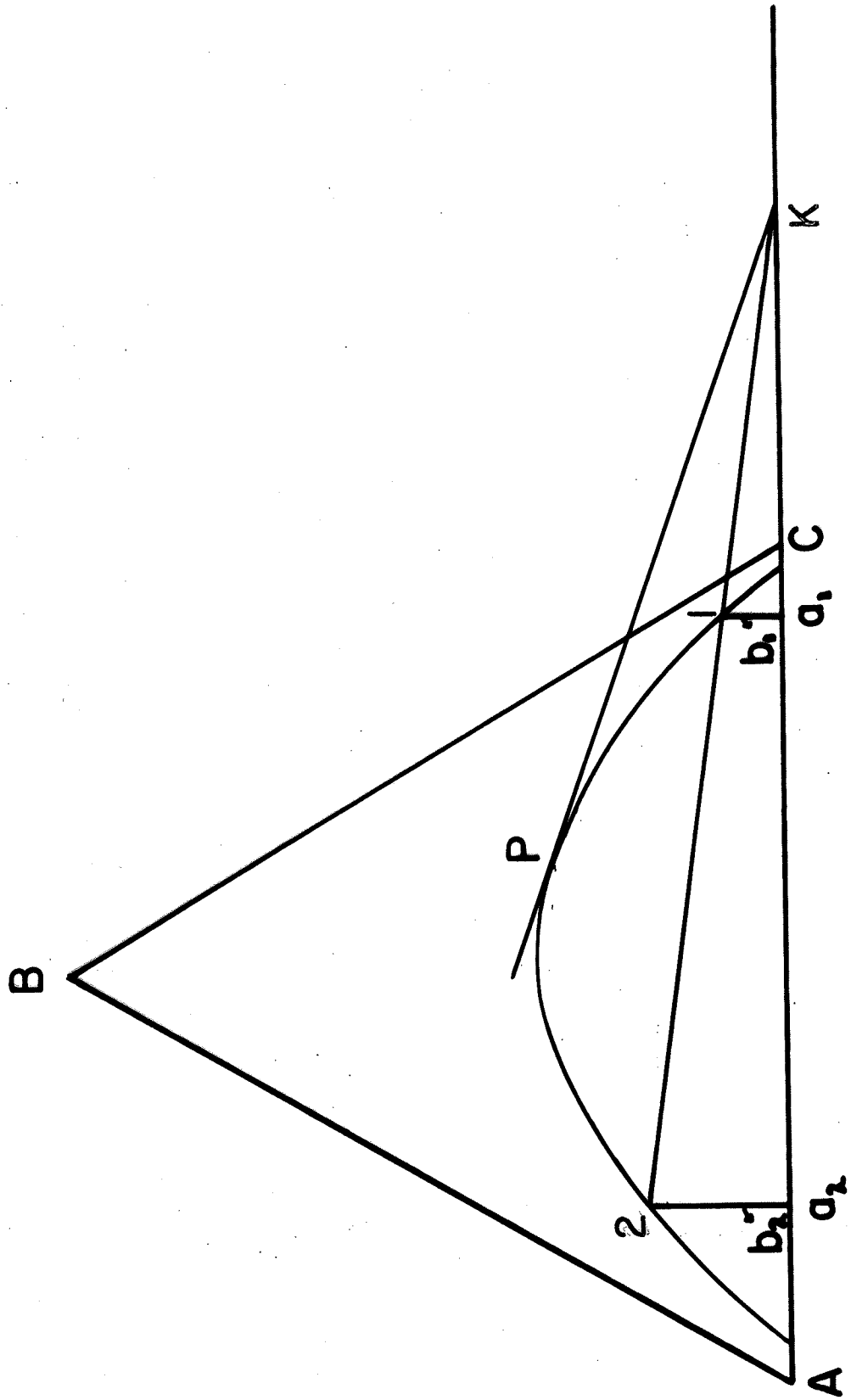
$a_2$  = concentration of A in 2

$b_1$  = concentration of B in 1

$b_2$  = concentration of B in 2

The origin is chosen at C





EXPERIMENTAL PROCEDURE AND APPARATUS

A. PURIFICATION OF THE MATERIALS(1) ACETIC ACID

Use was made of C.P. reagent acetic acid from the Canadian Industries Limited, the strength of which is a minimum of 99.8%.

The further purification was carried out by means of distillation after addition of 5 millilitres acetic anhydride (practical) to one litre of acetic acid. The product so obtained shows a density of  $d_4^{25} = 1.0441$  and a freezing point of  $16.4^{\circ}\text{C}$ . The freezing point of purest acetic acid, obtained by means of multiple freezing out methods is found to be  $16.63^{\circ}\text{C}$  by Wremsky et al<sup>14</sup>. Therefore the final product is of more than 99.9% purity.

(2) CHLOROFORM

Use was made of Chloroform (A.C.S.) from the Fisher Scientific Company.

Further purification was carried out as follows. One litre of chloroform was shaken with 50 ml. concentrated sulphuric acid. Afterwards the chloroform was washed with distilled water until no acid could be detected in the water(indicator). Finally the chloroform was dried over anhydrous calcium chloride. This chloroform was distilled over dry calcium chloride. The final product had the following physical

properties:  $d_4^{25} = 1.4806$  and  $n_D^{25} = 1.4433$ . The purity of this chloroform can be regarded as satisfactory. The literature values are:  $d_4^{25} = 1.4789$  and  $n_D^{25} = 1.4431$  according to Reinders and de Minjer<sup>34</sup>. According to the I.C.T. the  $d_4^{25}$  value lies between 1.4785 and 1.4799.

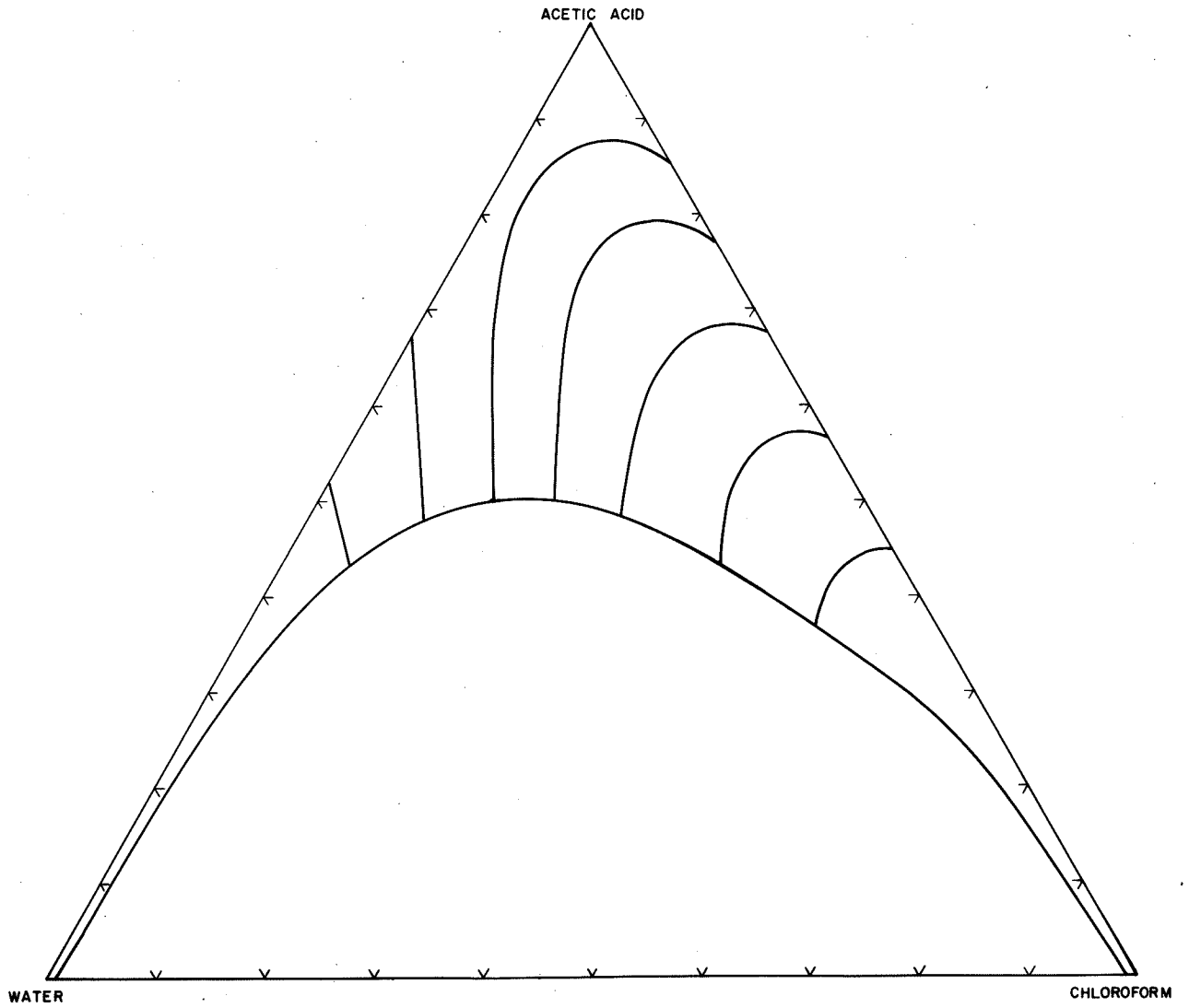
### (3) WATER

Distilled water was obtained by means of the distillation of water in a Barnstead still, yielding water with a conductivity of  $5 \times 10^{-6}$  m hos/cm at 25°C.

### B. METHOD OF ANALYSIS

For the analysis of the compositions of the liquid mixtures use was made of their respective physical properties. The suitability of a certain physical property for analytical purposes depends on two factors: first, the accuracy with which this property can be measured, requiring a minimum amount of sample and secondly the degree of variation of the physical property with concentration. In a binary mixture this implies the slope of the curve in the case of a straight line relationship or the steepness of the curvature in the case of a non-linear relationship. In the case of a ternary mixture use is made of two physical properties. These properties are plotted on an equilateral triangle superimposed on the corresponding concentrations. It is possible to construct lines in the triangle linking the concentrations for which the value of a certain physical property is constant. These lines are called lines of equal magnitude. Some of these lines are represented in the diagram on page 30<sup>a</sup>, where lines of equal refractive index are plotted for the system Acetic acid-chloroform-water.

30a



... Suitable properties should be chosen, so that the lines of equal magnitude intersect each other at as large an angle as possible. The measurement of the two physical properties then allows of the determination from the point of intersection of the corresponding equal magnitude lines, of the concentrations of the ternary components.

In the present investigations use has been made of two physical properties

(i) the refractive index, measured by means of an Abbe refractometer using the sodium D line ( $5893\overset{\circ}{\text{A}}$ ). The refractometer was a product of the Officine Galileo in Italy. The accuracy of the instrument is  $\pm 0.0001$ .

(ii) the acidity, determined by means of titration with standard 0.2N-sodium hydroxide using phenolphthaleine as the indicator. The NaOH was repeatedly checked with potassium hydrogen phthalate, and kept free from carbon dioxide.

In the binary system chloroform-acetic acid the refractive index allows the concentration to be measured to 0.2 weight percent.

In the binary system acetic acid-water the refractive index allows a measurement of the concentration to 0.2% accuracy up to 70 percent acetic acid. At higher acid concentrations the refractive index curve exhibits a maximum

which makes the method unsuitable for the estimation of concentrations in that region. In this case use is made of the acidity of the water-acetic acid mixture for the determination of the concentration.

The ternary system was analysed by means of the refractive index and the acidity. The acidity lies on a straight line of constant acidity, which is parallel to the base of the equilateral triangle if pure acetic acid is taken to represent the top of the triangle. The equi-refractive index lines are constructed using the data which are presented in the results. The greatest accuracy can be obtained in the middle part of the triangle only, but by adding one or more of the components any mixture can be caused to have a composition somewhere in the middle region. When a sample has been obtained for analysis, that shows partial miscibility, use is made of acetic acid addition to render the sample completely miscible. The overall accuracy of this method is about  $\pm .5$  percent by weight, that means .5 on a basis of 100 percent.

### C. MEASUREMENTS OF THE DENSITIES

For the measurement of the densities a pycnometer of the Ostwald-Sprengel type was used as described by Daniels et al<sup>38</sup> (1949). The capacity of the bottles was approximately 45 mls. and they were calibrated by means of distilled water

at 25°C.

After filling, the pycnometer was suspended in a 10 litre water bath that was controlled to  $25.00^{\circ}\text{C} \pm 0.005$  using a toluene-mercury control and a thyatron tube. As heating device a hundred Watt light bulb was used. The temperature was read from a Beckmann thermometer which was standardized against a standard platinum resistance thermometer. After half an hour the volume was adjusted as described by Daniels et al<sup>38</sup>. After removal from the thermostat the pycnometer was dried and transferred to a two pan balance. After thirty minutes the pycnometer was weighed against an empty pycnometer, thus avoiding any buoyancy error. In this manner the densities were reproducible to  $\pm 0.0002$  gm/ml.

The density data were used for the calculation of the molar volume, where in the case of a ternary mixture the molar volume for example can be computed from

$$V_{\text{exp.}} = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{d} \quad (32)$$

while the ideal molar volume is equal to

$$V_{\text{id.}} = x_1 \frac{M_1}{d_1} + x_2 \frac{M_2}{d_2} + x_3 \frac{M_3}{d_3} \quad (33)$$



D. METHODS FOR THE DETERMINATION OF THE TOTAL VAPOURPRESSURE AND VAPOUR COMPOSITION(1) DEVELOPMENT OF THE METHOD

There are four general categories of methods for the determination of vapour pressures available

(i) the static method

(ii) the indirect method, which is unsuitable for isothermal work and will therefore not be discussed here

(iii) the differential method

(iv) the dynamic method.

A discussion of these various methods prior to the year 1927 is given by Pearce and Snow<sup>39</sup>.

Since that year various modifications of these four methods have been developed, mostly in such a way as to suit the needs for a particular study. A discussion of more recent apparatus is provided by Everett<sup>40</sup> (1953).

The static method for the measurement of vapour pressures makes use of a direct manometric technique and yields sufficiently accurate results, but has the disadvantage that it is difficult to obtain accurate information on the vapour composition.

The method which is most widely used for the measurement of vapour pressures is the dynamic method, which makes

use of the isothermal distillation of the liquid by means of the displacement by air of the vapour in equilibrium with the liquid. Another method which is dynamic in nature, makes use of isothermal recycling stills, but this method is not very reliable according to Everett<sup>40</sup>. Often isothermal vapour pressure and vapour composition data are obtained from isobaric data at different external pressures. The data obtained in this way are usually not very reliable.

The method based on the isothermal distillation by means of air displacement will be described in more detail. This method is based on Dalton's Law of partial pressures. The essential features of the method are as follows:

(i) a measured volume of air is saturated with vapour by passing the air over the surface of, or bubbling it through, the liquid contained in the saturator

(ii) the weight of the liquid evaporated is determined by the loss in weight of the saturator, or the gain in weight of an absorber which removes the vapour from the effluent air

(iii) the total pressure exerted by the gaseous mixture in contact with the liquid is obtained from barometer and manometer readings.

From the data so obtained the partial vapour pressures may be calculated.

Wremsky<sup>41</sup> (1934) provides the exact formulae which can be used in the case of a mixture of two volatile components. The partial pressures can then be calculated according to his formulae.

Pearce and Snow<sup>40</sup> point out that this method has a few sources of error, which however, can lead to serious deviations. One of the main errors lies in the fact that it is very difficult to measure accurately and at the same time conveniently, the large volume of air required for a single determination. The error thus introduced will be greater or smaller depending upon the magnitude of the vapour pressure of the mixture studied.

In view of the fact that at room temperature water and acetic acid have rather low vapour pressures, it would take about twenty-four hours to obtain a reasonable amount of distillate, when the air speed is 1 litre per hour. This makes it very difficult to measure the volume of air exactly. Therefore it was decided to follow the procedure as used by Parks and Chaffee<sup>42</sup> (1927), in which the vapour pressures are measured with a manometer (static method) and the vapour composition by means of isothermal distillation using the

air displacement method. This implies that the volume of air need not be measured.

## (2) DESCRIPTION OF THE MANOMETER

The total vapour pressures were measured using a manometer as shown in Figure 2. The bulb b has a volume of approximately 50 ml and can be filled through the tube a. The manometer arm e has a diameter larger than 10 mm. This means that there still can be a capillary depression of 0.2 mm. However, this error is obviated by the use of comparative techniques. The cathetometer is standardized against  $H_2O$  at  $25^\circ C$  or against  $CHCl_3$  at  $25^\circ C$  for which substances the vapour pressure is well known. All measurements are referred back to this standardization.

Measurements were made as follows: A pure liquid or a binary or ternary mixture is brought into the bulb b, while stopcock c is opened, so that d is in connection with b. Vacuum suction is applied to the manometer via a. The liquid is frozen out by means of an acetone-dry ice mixture or with liquid nitrogen under continuous suction. The mercury in the arms d and e will come to equal level and stopcock c can be closed. The bulb b is brought to room temperature and again frozen out. After repeating this procedure several times, thus securing expulsion of dissolved air, the liquid is frozen out once more and tube a is sealed off in vacuo. As soon as the manometer has reached room temperature it is immersed completely in a thermostat of plexiglass (20 litres capacity). The temperature of the water in the thermostat was controlled at  $25.00^\circ C \pm 0.005$  by means of a mercury-toluene regulator

LEGEND TO FIGURE 2

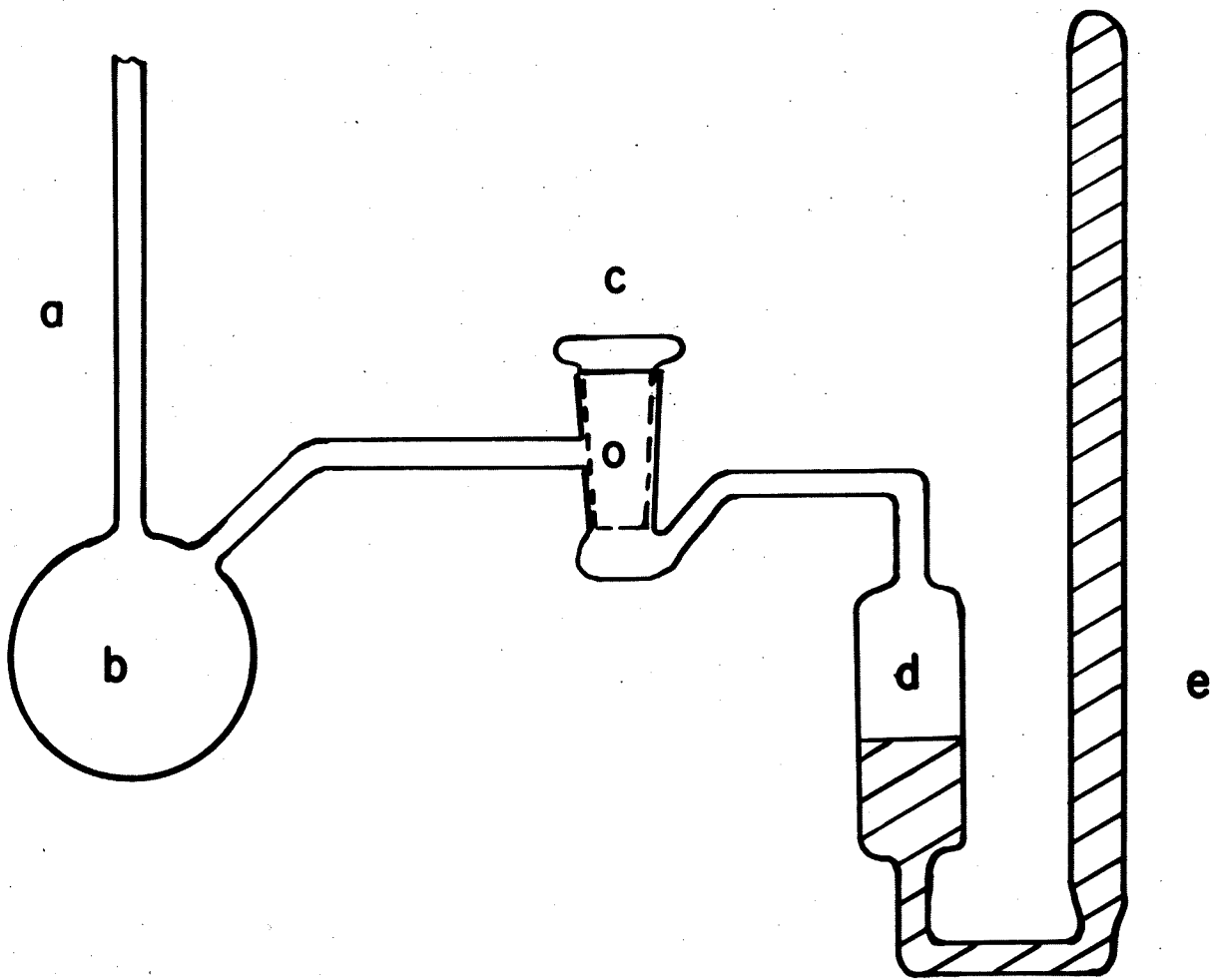
THE MANOMETER

a: Filling Tube

b: Bulb for Liquid Mixture

c: Vacuum Stop Cock

d + e: Manometer Arms



combined with a thyatron electronic tube and a 100 watt bulb as heating element. After allowing the manometer to obtain the temperature of the thermostat the stopcock c is opened and after an equilibration period of half an hour the difference in the mercury levels in the manometer arms was measured by means of a cathetometer. The readings are reduced to zero degrees centigrade making corrections for the expansions of the material of the cathetometer scale and the mercury, using the formula

$$b_0 = \frac{1 + \beta t_1}{1 + \alpha t_2} b$$

where  $b_0$  = reduced reading

$b$  = reading of cathetometer at  $t_1$ °C

$\alpha$  = 0.0001818, expansion coefficient of mercury

$\beta$  =  $10.5 \times 10^{-6}$ , expansion coefficient of steel.

In the case of the system water-acetic acid use is made of a cathetometer reading to 0.001 cm. However, due to a parallax effect the reading cannot be regarded to be more accurate than  $\pm .05$  mm. The cathetometer readings were standardized against the vapour pressure of water at 25°C (23.8 mm Hg).

In the cases of the system acetic acid-chloroform where the vapour pressures are higher and the ternary

system a large kathetometer is used giving an accuracy of  $\pm 0.2$  mm. This kathetometer is standardized against pure chloroform at  $25^{\circ}\text{C}$  (199.1 mm Hg).

### (3) APPARATUS FOR THE ISOTHERMAL DISTILLATION

The apparatus used for the determination of the composition of the vapour that is in equilibrium with a liquid mixture is represented in Figure 3.

Use was made of saturators as described by Pearce and Snow<sup>39</sup> and by Bichowski and Stork<sup>43</sup> (1915).

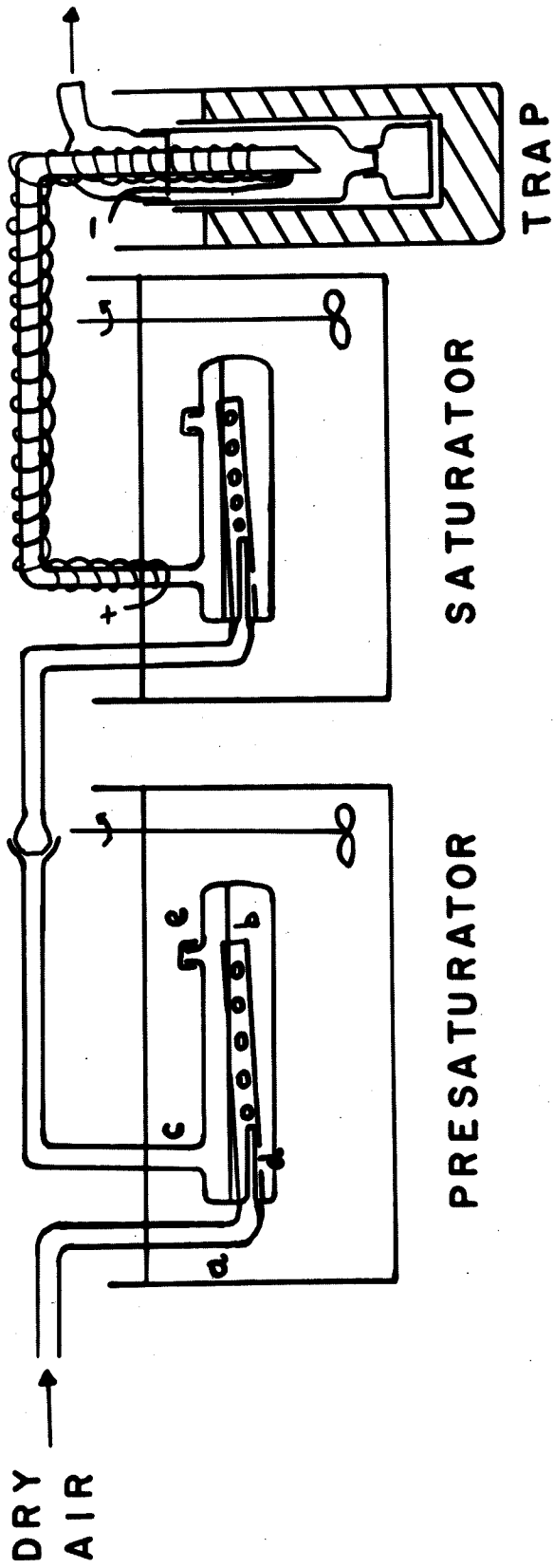
The saturators consist of a series of four units in the presaturator and eight units in the saturator part of the apparatus. Each unit is constructed as follows. The air enters the unit through a short central tube "a" tapered down to a 2 mm capillary. At the tip of the capillary the air breaks into bubbles which pass up a slightly inclined glass tube with inner diameter of 5 mm and about 80 mm long. The bubbles break at the end of the tube. The air then passes over the surface to the tube "c" and goes to the next saturator unit. An opening "d" is blown in the lower side of the inclined tube, just behind the capillary. Through this opening liquid is drawn from the bottom of saturator and carried by the gas bubbles up the slanting tube to the surface of the liquid. This



LEGEND TO FIGURE 3

The Isothermal Distillation Apparatus

- a: Air Inlet Tube
- b: Slanting Tube
- c: Outlet Tube
- d: Hole in Slanting Tube
- e: Filling Tube (Glass Stoppered)



insures a practically uniform concentration in the mixture. Each unit in a saturator is provided with an opening (e), which can be closed with a water tight ground glass joint. This makes filling easy. Each unit contains about 35 ml of liquid when filled.

The fact that the bubbles only have a short vertical movement in the liquid, while the contact with the liquid is comparatively long, ensures that when the bubble leaves the liquid surface the bubble will still be very nearly saturated. Complete saturation is insured because the air passes again over the liquid surface before entering the next unit.

The general procedure of a distillation will be described with reference to Figure 3. The compressed air is dried and purified from  $\text{CO}_2$  by passing it through a concentrated potassium-hydroxide solution, a concentrated sulphuric acid solution and an anhydrous calcium chloride tube respectively. The air then enters the presaturator, which consists of a series of four units, as described. This presaturator is completely immersed in a thermostat of 35 litres capacity, filled with water. The temperature is kept at  $30^\circ\text{C} \pm 0.05$ .

After having passed through the presaturator the air goes through a tube (at room temperature) to the

saturation. The saturator consists of eight absorption units and is completely immersed in a water bath of 35 litres capacity. The temperature is kept at  $25.00^{\circ}\text{C} \pm 0.01$  using a mercury-toluene control and a thyratron tube. As heating element a 200 Watt light bulb was used. The temperature was measured by means of a Beckmann thermometer standardized against a standard platinum resistance thermometer.

After leaving the last unit the air passes into a tube leading to the trap. In order to avoid condensation of the vapour in this tube a Ni-chrome resistance wire is wound around this tube right into the trap as is shown in Figure 3. The resistance wire is heated by means of a current supplied by a six volts copper oxide rectifier and gives a temperature of about  $50$  to  $60^{\circ}\text{C}$  in the tube. The trap consists of a glass tube 160 mm in length and 30 mm in diameter, which can be removed from the tube that is attached to the saturator, by means of a ground glass joint. The tubing coming from the saturator goes down to 10 mm from the bottom in this wide tube. The bottom end of the trap is connected to a weighing bottle via a ground glass joint. This weighing bottle has a capacity of 10 millilitres. The trap is surrounded by a glass tube and put into an acetone dry ice mixture in a Dewar flask, having a

temperature of  $-80^{\circ}\text{C}$ . After the distillation and the thawing of the condensate in the trap, this liquid is caught into the weighing bottle and analysed.

In the literature it is reported that air speeds up to ten litres per hour still give satisfactory saturation of the air. However, in this research a speed not exceeding two litres per hour was used. The results obtained for speeds varying between 0.5 and 2.0 litres/hour show no larger deviation than the experimental error, which is less than 1% by weight.

RESULTS AND TREATMENT OF THE DATA

A. VOLUME RESULTS(1) THE SYSTEM WATER-ACETIC ACID

The measurements carried out in this laboratory are presented in Table 1, giving the concentration of acetic acid in weight percent and mole percent. The density, the specific volume and the molar excess volume at 25°C are also reported.

The molar excess volumes have also been calculated from the data of Kohner and Gressmann<sup>25</sup> and Woodman<sup>24</sup>. The  $V^E$  results are plotted in Figure 4, showing a minimum of -1.145 millilitres at 0.5 mole fraction acetic acid.

From our own density data and those of Woodman and Kohner and Gressmann and also of Redlich and Nielsen<sup>26</sup>, the partial molal volumes were calculated. The data are represented in Table 2, giving the partial volumes for the concentrations of acetic acid in mole fraction. The partial molal excess volumes are also presented in Figure 5.

(2) THE SYSTEM CHLOROFORM-ACETIC ACID

In Table 3 the concentrations of chloroform are reported in weight percentage and mole percentage. The density, the specific volume and the excess volume at 25°C are also given. The excess volumes are plotted in Figure 6 as a function of the concentration. A maximum value for

$V^E$  of 0.555 ml exists at 0.45 mole fraction chloroform.

The partial molal volumes were calculated. From the curves thus obtained the partial molal volumes have been interpolated as reported in Table 4. In Figure 6 the partial molal excess volumes are plotted as a function of the concentration of chloroform expressed in mole fraction.

### (3) THE SYSTEM CHLOROFORM-ACETIC ACID-WATER

In Table 5 the density data and excess molar volumes are reported with the corresponding concentrations of the three components in weight and mole percentages. The results represented by numbers 71 - 78 are obtained indirectly by means of corresponding points from a ternary plot of the density data against the concentrations. These points were indispensable because otherwise too few data would be available for the plotting of excess functions with positive values.

The excess volumes were plotted as functions of the composition of the ternary system, at the same time making use of the binary data. The miscibility gap was constructed from the data of Wright et al<sup>32</sup> and Brancker et al<sup>33</sup>. From this plot the equi-excess volume lines as presented in Figure 8 were interpolated.

From Figure 8 it follows that from the concentration



of 100 mole percent acetic acid to 100 mole percent chloroform there is a line where the excess molar volume is equal to zero.

TABLE 1  
DENSITY DATA FOR SYSTEM H<sub>2</sub>O-HA<sub>c</sub>

| Wt. % HA <sub>c</sub> | Mole % HA <sub>c</sub> | $d_4^{25}$ | s.v. ml <sup>-1</sup> | $V^E$ ml<br>(negative) |
|-----------------------|------------------------|------------|-----------------------|------------------------|
| 100.00                | 100.00                 | 1.0440     | .9577                 | —                      |
| 96.06                 | 87.97                  | 1.0535     | .9493                 | 0.571                  |
| 93.75                 | 81.82                  | 1.0567     | .9464                 | 0.751                  |
| 89.32                 | 71.51                  | 1.0611     | .9424                 | 0.974                  |
| 84.93                 | 62.84                  | 1.0636     | .9402                 | 1.088                  |
| 78.96                 | 52.97                  | 1.0648     | .9391                 | 1.137                  |
| 69.31                 | 40.39                  | 1.0635     | .9402                 | 1.101                  |

LEGEND TO FIGURE 4

The Excess Volume Function For The  
System Acetic Acid-Water at 25°C

× Kohner and Gressmann

● Woodman

○ This Research

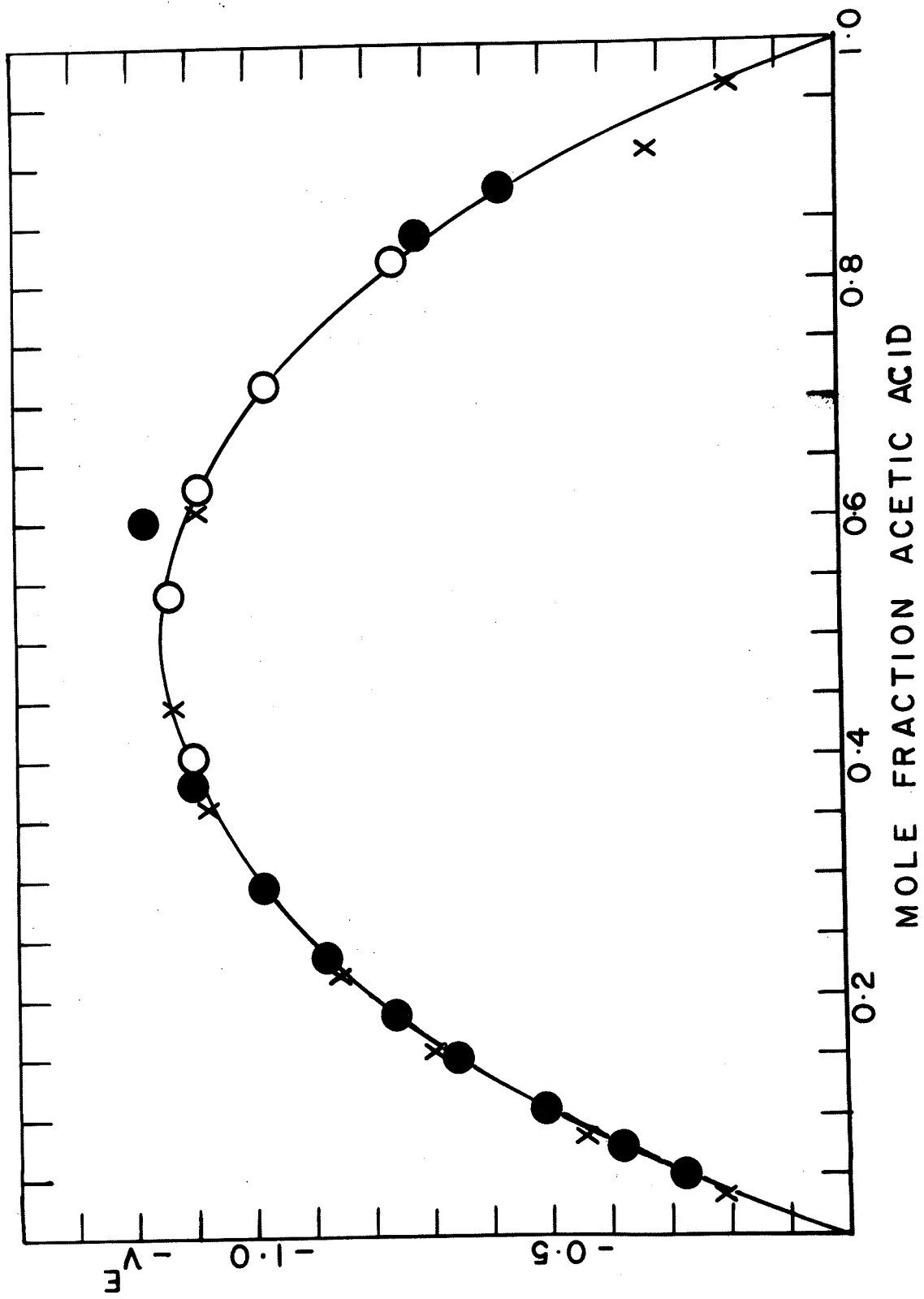


TABLE 2

PARTIAL MOLAL VOLUMES IN THE  
SYSTEM ACETIC ACID-WATER

| Mole fraction<br>$\text{HA}_c$ | $v_{\text{HA}_c}$ | $v_{\text{HA}_c} - v_{\text{HA}_c}^0$<br>(negative) | $v_{\text{H}_2\text{O}}$ | $v_{\text{H}_2\text{O}} - v_{\text{H}_2\text{O}}^0$<br>(negative) |
|--------------------------------|-------------------|---|--------------------------|---|
| 0.0                            | 51.88             | 5.63  | 18.07                    | 0.00  |
| 0.1                            | 53.37             | 4.14  | 17.95                    | 0.12  |
| 0.2                            | 54.53             | 2.98  | 17.78                    | 0.29  |
| 0.3                            | 55.38             | 2.13  | 17.57                    | 0.50  |
| 0.4                            | 55.98             | 1.53  | 17.29                    | 0.78  |
| 0.5                            | 56.40             | 1.11  | 16.92                    | 1.15  |
| 0.6                            | 56.74             | 0.77  | 16.47                    | 1.60  |
| 0.7                            | 52.02             | 0.49  | 15.90                    | 2.17  |
| 0.8                            | 57.24             | 0.27  | 15.19                    | 2.88  |
| 0.9                            | 57.39             | 0.12  | 14.01                    | 4.06  |
| 1.0                            | 57.51             | 0.00  | 12.71                    | 5.36  |

LEGEND TO FIGURE 5

The Partial Molal Excess Volumes  
In The System Acetic Acid-Water at 25°C

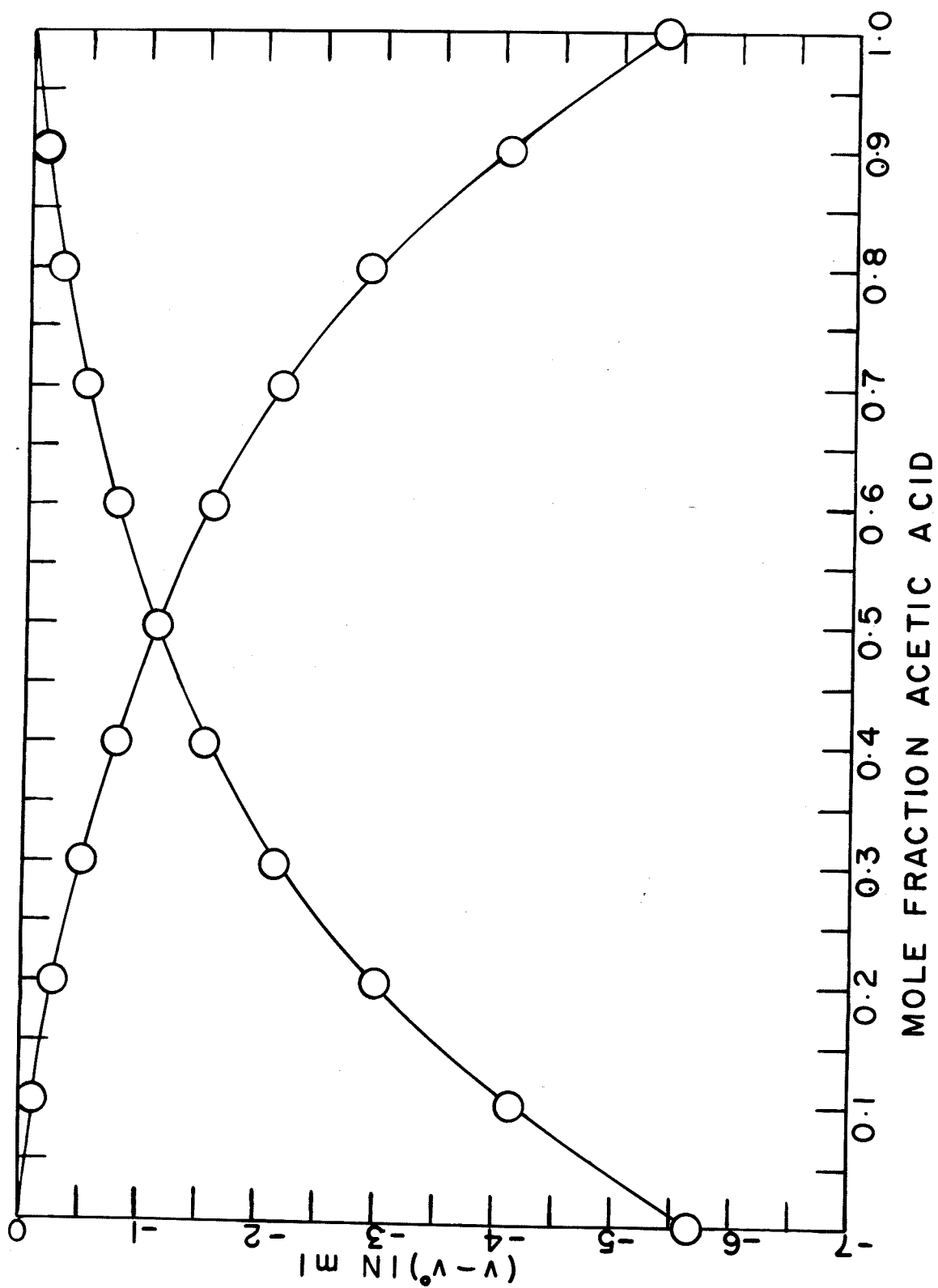


TABLE 3DENSITY DATA FOR THE SYSTEM HA<sub>c</sub>-CHCl<sub>3</sub>

| Wt. % CHCl <sub>3</sub> | Mole % CHCl <sub>3</sub> | $d_4^{25}$ | s.v. ml <sup>-1</sup> | $V^E$ ml |
|-------------------------|--------------------------|------------|-----------------------|----------|
| 0.00                    | 0.00                     | 1.0440     | .9579                 | 0.000    |
| 2.83                    | 1.44                     | 1.0522     | .9504                 | 0.033    |
| 14.80                   | 8.03                     | 1.0879     | .9192                 | 0.204    |
| 26.70                   | 15.48                    | 1.1279     | .8866                 | 0.286    |
| 37.84                   | 23.44                    | 1.1668     | .8570                 | 0.447    |
| 49.74                   | 33.23                    | 1.2141     | .8237                 | 0.504    |
| 59.86                   | 42.86                    | 1.2574     | .7953                 | 0.555    |
| 69.39                   | 53.27                    | 1.3035     | .7672                 | 0.486    |
| 76.03                   | 61.47                    | 1.3366     | .7482                 | 0.489    |
| 82.76                   | 70.71                    | 1.3738     | .7279                 | 0.386    |
| 89.65                   | 81.33                    | 1.4118     | .7083                 | 0.397    |
| 93.89                   | 88.54                    | 1.4408     | .6941                 | 0.157    |
| 100.00                  | 100.00                   | 1.4806     | .6754                 | 0.000    |



LEGEND TO FIGURE 6

The Excess Volume Function in the System

Acetic Acid-Chloroform at 25°C

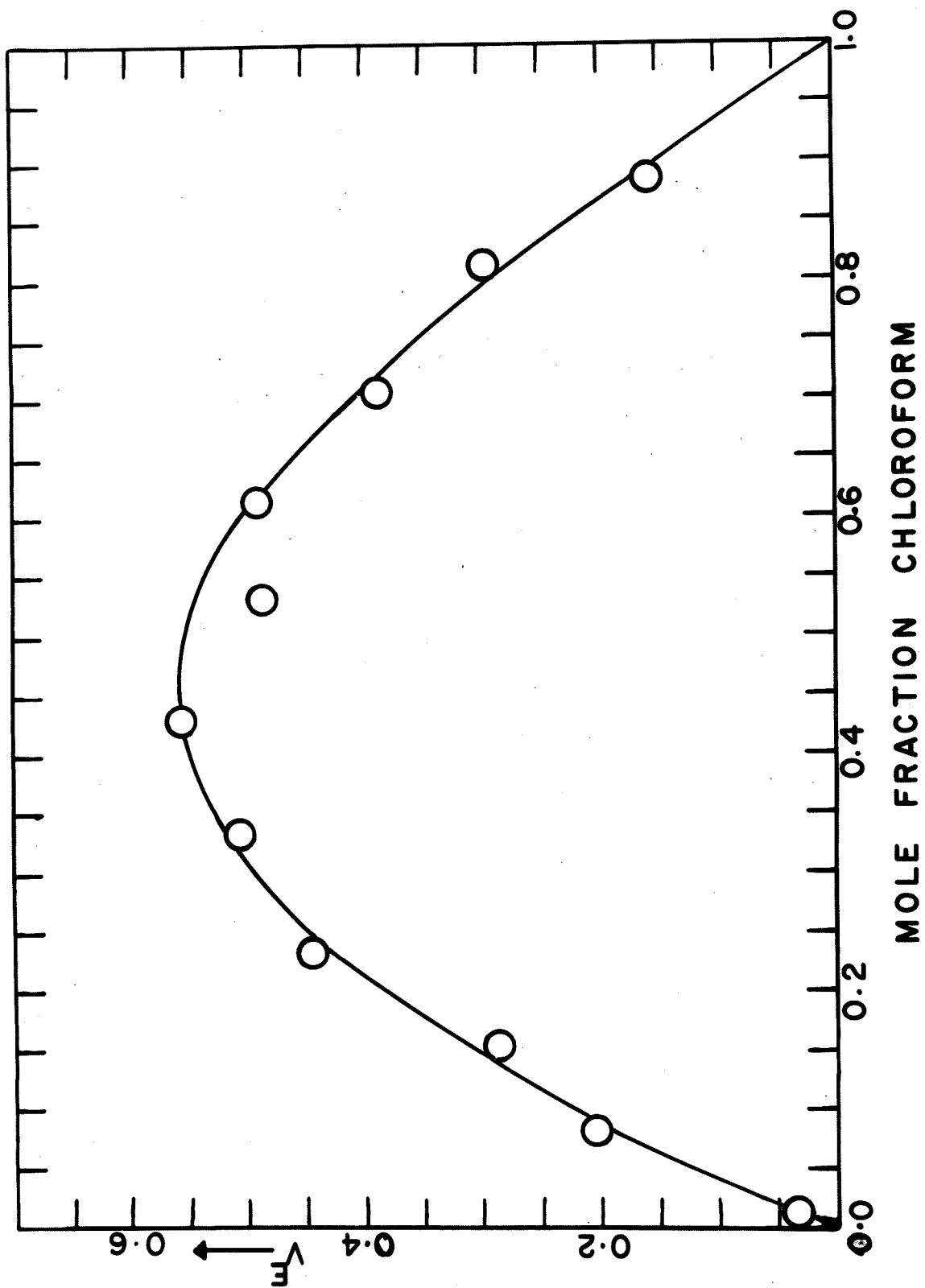


TABLE 4

PARTIAL MOLAL VOLUMES IN THE SYSTEMACETIC ACID-CHLOROFORM

| Mole fraction<br>$\text{CHCl}_3$ | $v_{\text{CHCl}_3}$<br>ml | $(v - v^0)_{\text{CHCl}_3}$<br>ml | $v_{\text{HA}_c}$<br>ml | $(v - v^0)_{\text{HA}_c}$<br>ml |
|----------------------------------|---------------------------|-----------------------------------|-------------------------|---------------------------------|
| 0.0                              | 83.86                     | 3.22                              | 57.51                   | 0.00                            |
| 0.1                              | 82.66                     | 2.02                              | 57.54                   | 0.03                            |
| 0.2                              | 82.09                     | 1.45                              | 57.64                   | 0.11                            |
| 0.3                              | 81.68                     | 1.02                              | 57.78                   | 0.27                            |
| 0.4                              | 81.33                     | 0.69                              | 57.95                   | 0.44                            |
| 0.5                              | 81.06                     | 0.42                              | 58.15                   | 0.64                            |
| 0.6                              | 80.88                     | 0.22                              | 58.40                   | 0.89                            |
| 0.7                              | 80.77                     | 0.13                              | 58.67                   | 1.16                            |
| 0.8                              | 80.71                     | 0.07                              | 59.01                   | 1.50                            |
| 0.9                              | 80.67                     | 0.03                              | 59.35                   | 1.84                            |
| 1.0                              | 80.64                     | 0.00                              | 59.69                   | 2.18                            |

LEGEND TO FIGURE 7

The Partial Molal Excess Volumes in the System

Acetic Acid-Chloroform at 25°C

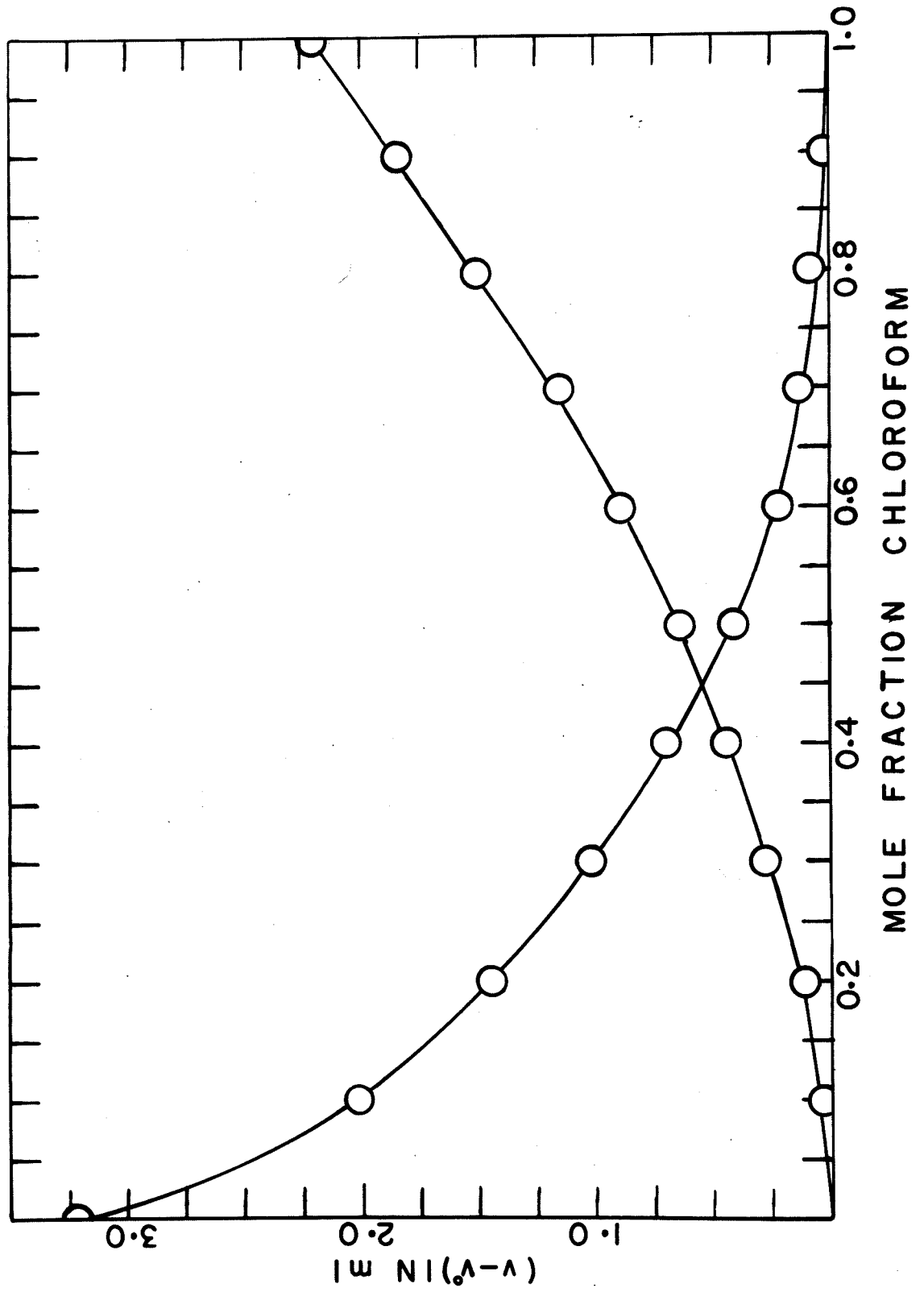


TABLE 5

DENSITY DATA FOR THE SYSTEMWATER-ACETIC ACID-CHLOROFORM

| No. | H <sub>2</sub> O |        | HA <sub>c</sub> |        | CHCl <sub>3</sub> |        | d <sub>4</sub> <sup>25</sup> | V <sup>E</sup> ★<br>ml |
|-----|------------------|--------|-----------------|--------|-------------------|--------|------------------------------|------------------------|
|     | Wt. %            | Mole % | Wt. %           | Mole % | Wt. %             | Mole % |                              |                        |
| 1   | 9.76             | 31.60  | 50.34           | 48.91  | 39.90             | 19.49  | 1.1913                       | 0.593                  |
| 2   | 20.99            | 51.06  | 54.97           | 40.12  | 24.04             | 8.82   | 1.1376                       | 0.804                  |
| 3   | 30.43            | 60.86  | 60.82           | 36.50  | 8.75              | 2.64   | 1.0885                       | 1.016                  |
| 4   | 5.52             | 21.40  | 40.35           | 46.94  | 54.13             | 31.66  | 1.2447                       | 0.285                  |
| 5   | 10.89            | 31.68  | 67.32           | 58.76  | 21.79             | 9.56   | 1.1286                       | 0.795                  |
| 6   | 20.43            | 49.06  | 61.71           | 44.47  | 17.86             | 6.47   | 1.1181                       | 0.997                  |
| 7   | 10.68            | 30.70  | 71.23           | 61.45  | 18.09             | 7.85   | 1.1164                       | 0.882                  |
| 8   | 19.05            | 47.59  | 58.75           | 44.04  | 22.20             | 8.37   | 1.1319                       | 0.911                  |
| 9   | 20.50            | 50.51  | 54.24           | 40.10  | 25.26             | 9.39   | 1.1416                       | 0.878                  |
| 10  | 9.91             | 29.89  | 64.68           | 58.54  | 25.41             | 11.57  | 1.1403                       | 0.739                  |
| 11  | 9.98             | 31.42  | 54.94           | 51.91  | 35.08             | 16.67  | 1.1738                       | 0.644                  |
| 12  | 14.81            | 43.12  | 44.79           | 39.13  | 40.40             | 17.75  | 1.1941                       | 0.680                  |
| 13  | 8.07             | 29.40  | 36.89           | 40.33  | 55.04             | 30.26  | 1.2502                       | 0.404                  |
| 14  | 1.95             | 9.53   | 24.87           | 36.48  | 73.18             | 53.99  | 1.3282                       | +0.080                 |
| 15  | 9.48             | 33.08  | 37.00           | 38.74  | 53.52             | 28.18  | 1.2444                       | 0.462                  |
| 16  | 13.18            | 34.91  | 76.94           | 61.14  | 9.88              | 3.95   | 1.0921                       | 0.964                  |
| 17  | 50.11            | 77.95  | 44.58           | 20.81  | 5.31              | 1.24   | 1.0672                       | 0.798                  |
| 18  | 5.50             | 16.61  | 89.57           | 81.15  | 4.93              | 2.24   | 1.0707                       | 0.677                  |
| 19  | 3.98             | 12.21  | 94.73           | 87.19  | 1.29              | 0.59   | 1.0572                       | 0.559                  |

contd.

TABLE 5 CONTD.

| No. | H <sub>2</sub> O |        | HA <sub>c</sub> |        | CHCl <sub>3</sub> |        | d <sub>4</sub> <sup>25</sup> | v <sup>E</sup> ★<br>ml |
|-----|------------------|--------|-----------------|--------|-------------------|--------|------------------------------|------------------------|
|     | Wt. %            | Mole % | Wt. %           | Mole % | Wt. %             | Mole % |                              |                        |
| 20  | 53.22            | 79.38  | 45.38           | 20.31  | 1.40              | 0.32   | 1.0547                       | 0.799                  |
| 21  | 57.50            | 82.16  | 40.72           | 17.46  | 1.78              | 0.38   | 1.0519                       | 0.915                  |
| 22  | 62.97            | 85.23  | 35.73           | 14.51  | 1.30              | 0.26   | 1.0443                       | 0.611                  |
| 23  | 17.99            | 43.28  | 75.06           | 54.19  | 6.95              | 2.52   | 1.0847                       | 1.061                  |
| 24  | 67.40            | 87.61  | 30.94           | 12.07  | 1.66              | 0.32   | 1.0419                       | 0.559                  |
| 25  | 60.58            | 83.94  | 37.80           | 15.72  | 1.62              | 0.34   | 1.0489                       | 0.679                  |
| 26  | 57.63            | 82.21  | 40.72           | 17.43  | 1.65              | 0.36   | 1.0516                       | 0.733                  |
| 27  | 61.39            | 84.65  | 35.56           | 14.71  | 3.05              | 0.64   | 1.0516                       | 0.643                  |
| 28  | 45.84            | 74.66  | 49.50           | 24.19  | 4.66              | 1.15   | 1.0687                       | 0.869                  |
| 29  | 32.89            | 13.25  | 64.20           | 86.17  | 2.91              | 0.59   | 1.0711                       | 1.086                  |
| 30  | 5.17             | 16.47  | 79.90           | 76.36  | 14.93             | 7.17   | 1.1007                       | 0.547                  |
| 31  | 9.76             | 28.15  | 75.69           | 65.52  | 14.54             | 6.33   | 1.1045                       | 0.819                  |
| 32  | 9.64             | 27.29  | 80.74           | 68.60  | 9.62              | 4.11   | 1.0890                       | 0.856                  |
| 33  | 7.09             | 20.94  | 85.49           | 75.76  | 7.42              | 3.30   | 1.0798                       | 0.747                  |
| 34  | 25.96            | 54.54  | 70.15           | 44.23  | 3.89              | 1.23   | 1.0758                       | 1.101                  |
| 35  | 34.49            | 64.63  | 60.27           | 33.89  | 5.24              | 1.48   | 1.0769                       | 1.013                  |
| 36  | 12.78            | 33.46  | 82.12           | 64.52  | 5.10              | 2.02   | 1.0775                       | 0.995                  |
| 37  | 14.72            | 37.60  | 77.52           | 59.41  | 7.76              | 2.99   | 1.0863                       | 1.012                  |
| 38  | 9.99             | 27.57  | 84.85           | 70.28  | 5.16              | 2.15   | 1.0758                       | 0.909                  |
| 39  | 25.09            | 55.32  | 60.07           | 39.74  | 14.84             | 4.94   | 1.1081                       | 0.985                  |
| 40  | 21.70            | 50.17  | 65.30           | 45.30  | 12.99             | 4.53   | 1.1030                       | 1.015                  |

contd.

TABLE 5 CONTD.

| No. | H <sub>2</sub> O |        | HA <sub>c</sub> |        | CHCl <sub>3</sub> |        | d <sub>4</sub> <sup>25</sup> | v <sup>E</sup> ★<br>ml |
|-----|------------------|--------|-----------------|--------|-------------------|--------|------------------------------|------------------------|
|     | Wt. %            | Mole % | Wt. %           | Mole % | Wt. %             | Mole % |                              |                        |
| 41  | 30.05            | 61.57  | 55.00           | 33.81  | 14.95             | 4.62   | 1.1066                       | 0.944                  |
| 42  | 26.69            | 57.15  | 60.01           | 38.56  | 13.30             | 4.30   | 1.1031                       | 0.993                  |
| 43  | 21.14            | 49.24  | 66.30           | 46.34  | 12.56             | 4.42   | 1.1017                       | 1.016                  |
| 44  | 14.95            | 41.50  | 55.24           | 46.01  | 29.81             | 12.49  | 1.1570                       | 0.803                  |
| 45  | 10.61            | 32.12  | 59.89           | 54.40  | 29.50             | 13.48  | 1.1545                       | 0.717                  |
| 46  | 9.57             | 31.86  | 45.74           | 45.69  | 44.69             | 22.45  | 1.2095                       | 0.549                  |
| 47  | 5.02             | 18.67  | 50.49           | 56.35  | 44.49             | 24.97  | 1.2051                       | 0.311                  |
| 48  | 4.43             | 16.74  | 50.99           | 57.83  | 44.58             | 25.43  | 1.2047                       | 0.262                  |
| 49  | 5.16             | 19.65  | 45.51           | 52.00  | 49.33             | 28.35  | 1.2244                       | 0.281                  |
| 50  | 5.67             | 21.21  | 45.78           | 51.39  | 48.55             | 27.40  | 1.2220                       | 0.335                  |
| 51  | 4.92             | 20.06  | 35.29           | 43.16  | 59.79             | 36.78  | 1.2686                       | 0.215                  |
| 52  | 4.25             | 13.07  | 92.69           | 85.51  | 3.06              | 1.42   | 1.0628                       | 0.565                  |
| 53  | 38.66            | 69.59  | 51.21           | 27.66  | 10.13             | 2.75   | 1.0884                       | 0.905                  |
| 54  | 25.62            | 56.92  | 54.76           | 36.50  | 19.62             | 6.58   | 1.1223                       | 0.917                  |
| 55  | 36.98            | 66.75  | 59.73           | 32.35  | 3.29              | 0.90   | 1.0703                       | 1.004                  |
| 56  | 22.08            | 52.03  | 57.67           | 40.77  | 20.25             | 7.20   | 1.1253                       | 0.932                  |
| 57  | 15.03            | 41.14  | 58.19           | 47.80  | 26.77             | 11.06  | 1.1467                       | 0.835                  |
| 58  | 20.21            | 50.71  | 50.98           | 38.38  | 28.81             | 10.91  | 1.1530                       | 0.827                  |
| 59  | 26.33            | 57.67  | 55.02           | 36.16  | 18.65             | 6.16   | 1.1181                       | 0.897                  |
| 60  | 34.98            | 66.52  | 52.26           | 29.82  | 12.76             | 3.66   | 1.0978                       | 0.914                  |
| 61  | 45.28            | 74.61  | 47.98           | 23.72  | 6.73              | 1.67   | 1.0747                       | 0.855                  |

contd.



TABLE 5 CONTD.

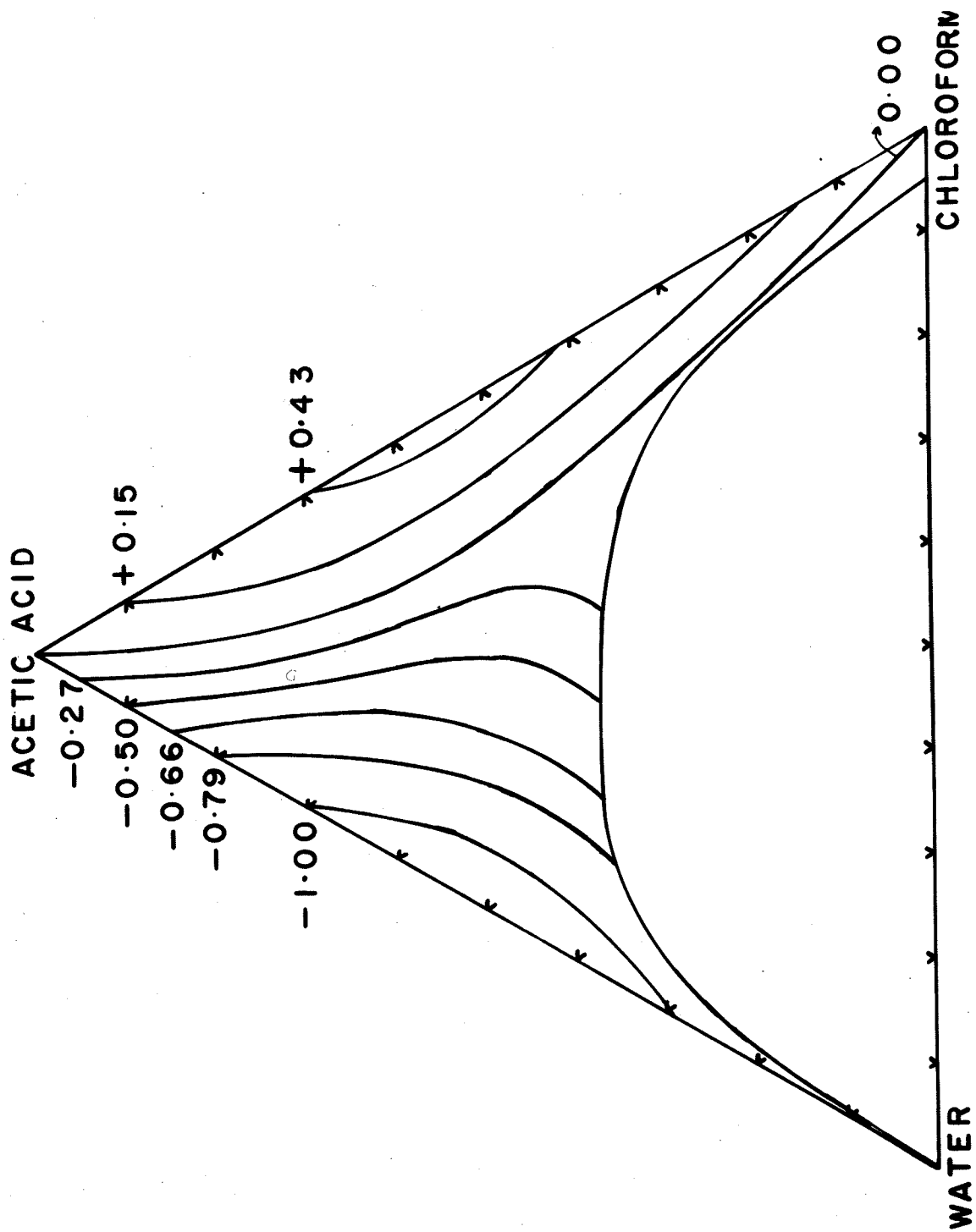
| No. | H <sub>2</sub> O |        | HA <sub>c</sub> |        | CHCl <sub>3</sub> |        | d <sub>4</sub> <sup>25</sup> | v <sup>E</sup> ★<br>ml |
|-----|------------------|--------|-----------------|--------|-------------------|--------|------------------------------|------------------------|
|     | Wt. %            | Mole % | Wt. %           | Mole % | Wt. %             | Mole % |                              |                        |
| 62  | 30.70            | 62.64  | 52.65           | 32.23  | 16.65             | 5.13   | 1.1114                       | 0.913                  |
| 63  | 23.33            | 53.23  | 59.85           | 40.98  | 16.82             | 5.79   | 1.1144                       | 0.938                  |
| 64  | 42.07            | 71.82  | 52.06           | 26.67  | 5.87              | 1.51   | 1.0746                       | 0.913                  |
| 65  | 22.40            | 8.13   | 75.72           | 91.53  | 1.89              | 0.34   | 1.0702                       | 1.286                  |
| 66  | 29.70            | 58.78  | 68.52           | 40.69  | 1.78              | 0.53   | 1.0689                       | 1.093                  |
| 67  | 52.07            | 78.89  | 44.90           | 20.41  | 3.03              | 0.69   | 1.0600                       | 0.803                  |
| 68  | 28.52            | 58.45  | 63.63           | 39.13  | 7.85              | 2.43   | 1.0868                       | 1.048                  |
| 69  | 32.03            | 63.27  | 55.92           | 33.14  | 12.05             | 3.59   | 1.0976                       | 0.968                  |
| 70  | 43.57            | 72.19  | 55.42           | 27.56  | 1.01              | 0.25   | 1.0604                       | 0.945                  |
| 71  | 2.0              | 6.70   | 87.3            | 87.90  | 10.7              | 5.40   | 1.0798                       | 0.147                  |
| 72  | 2.0              | 6.85   | 83.1            | 85.45  | 14.9              | 7.70   | 1.0921                       | 0.063                  |
| 73  | 2.0              | 7.10   | 75.8            | 80.95  | 22.2              | 11.90  | 1.1144                       | +0.082                 |
| 74  | 2.0              | 7.25   | 72.5            | 78.80  | 25.5              | 13.95  | 1.1253                       | +0.125                 |
| 75  | 2.0              | 7.60   | 63.7            | 72.70  | 34.3              | 19.70  | 1.1570                       | +0.167                 |
| 76  | 2.0              | 8.05   | 54.3            | 65.45  | 43.7              | 26.50  | 1.1941                       | +0.154                 |
| 77  | 2.0              | 8.65   | 42.3            | 54.95  | 55.7              | 36.40  | 1.2444                       | +0.174                 |
| 78  | 2.0              | 8.95   | 37.1            | 49.85  | 60.9              | 41.15  | 1.2686                       | +0.123                 |

★ negative, unless stated otherwise

LEGEND TO FIGURE 8

The Excess Volume Functions in the System

Acetic Acid-Chloroform-Water at 25°C



B. REFRACTOMETRIC RESULTS(1) THE SYSTEM WATER-ACETIC ACID

The results of the measurements of the refractive indices in the system water-acetic acid are reported in Table 6 together with the molar refractions, which are calculated from the refractive indices and the densities. The latter are derived from a graph of the density versus concentration. The calculated molar refraction is also reported. Finally, the apparent molar refraction for acetic acid has been calculated according to the formula

$$\phi_R = \frac{R_{\text{exp.}} - x_1 R_1^0}{x_2}$$

where  $x_1$ ,  $R_1^0$  are the mole fraction and molar refraction of pure water respectively and  $x_2$  the mole fraction of acetic acid.

(2) THE SYSTEM ACETIC ACID-CHLOROFORM

The results of the measurements of the refractive indices in the system acetic acid-chloroform are reported in Table 7 together with the experimental and theoretical molar refractions, obtained in a similar fashion as in the system water-acetic acid. The apparent molar refraction of acetic acid has been calculated and is tabulated.

(3) THE SYSTEM WATER-ACETIC ACID-CHLOROFORM

The refractive indices are reported in Table 8. These refractive indices were plotted on an equilateral triangle. In this way lines of equal refractive index were obtained, and this provided a means for the determination of concentrations in ternary systems.

TABLE 6

REFRACTIVE PROPERTIES OF THE SYSTEMWATER-ACETIC ACID

| Weight %<br>HA <sub>c</sub> | Mole %<br>HA <sub>c</sub> | $n_D^{25.03}$ | $d_4^{25}$ | R exp. | R. calc. | $\phi_R$<br>HA <sub>c</sub> |
|-----------------------------|---------------------------|---------------|------------|--------|----------|-----------------------------|
| 0.00                        | 0.00                      | 1.3328        | 0.99707    | -      | 3.715    | -                           |
| 9.45                        | 3.04                      | 1.3395        | 1.0100     | 3.999  | 3.998    | 13.06                       |
| 18.60                       | 6.42                      | 1.3458        | 1.0218     | 4.315  | 4.312    | 13.07                       |
| 21.65                       | 7.66                      | 1.3480        | 1.0253     | 4.433  | 4.427    | 13.09                       |
| 27.07                       | 10.02                     | 1.3514        | 1.0320     | 4.651  | 4.647    | 13.05                       |
| 37.89                       | 15.47                     | 1.3585        | 1.0436     | 5.165  | 5.154    | 13.09                       |
| 45.89                       | 20.29                     | 1.3623        | 1.0504     | 5.609  | 5.602    | 13.05                       |
| 54.91                       | 26.76                     | 1.3668        | 1.0569     | 6.214  | 6.203    | 13.05                       |
| 62.53                       | 33.37                     | 1.3699        | 1.0610     | 6.828  | 6.818    | 13.05                       |
| 66.82                       | 37.67                     | 1.3718        | 1.0627     | 7.235  | 7.218    | 13.06                       |
| 70.21                       | 41.42                     | 1.3729        | 1.0638     | 7.584  | 7.566    | 13.06                       |
| 82.41                       | 58.53                     | 1.3759        | 1.0644     | 9.175  | 9.148    | 13.06                       |
| 84.69                       | 62.40                     | 1.3759        | 1.0637     | 9.541  | 9.518    | 13.05                       |
| 84.70                       | 62.42                     | 1.3761        | 1.0637     | 9.547  | 9.519    | 13.06                       |
| 87.06                       | 66.87                     | 1.3761        | 1.0626     | 9.961  | 9.933    | 13.06                       |
| 88.65                       | 70.09                     | 1.3757        | 1.0616     | 10.253 | 10.233   | 13.04                       |
| 90.90                       | 74.98                     | 1.3756        | 1.0598     | 10.713 | 10.687   | 13.05                       |
| 94.94                       | 84.92                     | 1.3743        | 1.0550     | 11.633 | 11.612   | 13.04                       |
| 96.94                       | 90.48                     | 1.3732        | 1.0516     | 12.147 | 12.129   | 13.03                       |
| 100.00                      | 100.00                    | 1.3702        | 1.0440     | -      | 13.014   | 13.01                       |

TABLE 7

REFRACTIVE PROPERTIES OF THE SYSTEMACETIC-ACID-CHLOROFORM

| Weight %<br>CHCl <sub>3</sub> | Mole %<br>ChCl <sub>3</sub> | $n_D^{25.03}$ | R. exp. | R. calc. | $\phi R_{HA_c}$ |
|-------------------------------|-----------------------------|---------------|---------|----------|-----------------|
| 0.00                          | 0.00                        | 1.3702        | -       | 13.014   | 13.01           |
| 3.63                          | 1.86                        | 1.3720        | 13.182  | 13.170   | 13.03           |
| 10.67                         | 5.67                        | 1.3753        | 13.508  | 13.489   | 13.03           |
| 12.98                         | 6.98                        | 1.3763        | 13.615  | 13.599   | 13.03           |
| 15.18                         | 8.26                        | 1.3772        | 13.719  | 13.760   | 13.03           |
| 28.69                         | 16.83                       | 1.3845        | 14.442  | 14.424   | 13.04           |
| 31.79                         | 18.99                       | 1.3865        | 14.638  | 14.605   | 13.06           |
| 38.97                         | 24.31                       | 1.3901        | 15.069  | 15.050   | 13.04           |
| 45.08                         | 29.22                       | 1.3942        | 15.497  | 15.461   | 13.06           |
| 45.32                         | 29.42                       | 1.3945        | 15.519  | 15.478   | 13.07           |
| 49.57                         | 33.08                       | 1.3970        | 15.820  | 15.785   | 13.07           |
| 49.70                         | 33.20                       | 1.3972        | 15.835  | 15.795   | 13.07           |
| 52.83                         | 36.03                       | 1.3993        | 16.069  | 16.032   | 13.07           |
| 71.18                         | 55.40                       | 1.4139        | 17.701  | 17.654   | 13.12           |
| 79.10                         | 65.56                       | 1.4210        | 18.554  | 18.505   | 13.16           |
| 87.31                         | 77.58                       | 1.4294        | 19.576  | 19.512   | 13.30           |
| 90.83                         | 83.28                       | 1.4329        | 20.035  | 19.990   | 13.28           |
| 100.00                        | 100.00                      | 1.4433        | -       | 21.390   |                 |

TABLE 8

REFRACTIVE PROPERTIES OF THE SYSTEMWATER-ACETIC ACID-CHLOROFORM

| No. | Weight %<br>H <sub>2</sub> O | Weight %<br>HA <sub>c</sub> | Weight %<br>CHCl <sub>3</sub> | n <sub>D</sub> <sup>25.03</sup> |
|-----|------------------------------|-----------------------------|-------------------------------|---------------------------------|
| 1   | 29.72                        | 62.23                       | 8.05                          | 1.3758                          |
| 2   | 42.39                        | 54.41                       | 3.19                          | 1.3688                          |
| 3   | 15.09                        | 56.34                       | 28.57                         | 1.3882                          |
| 4   | 9.73                         | 50.63                       | 39.64                         | 1.3943                          |
| 5   | 4.52                         | 39.54                       | 55.93                         | 1.4042                          |
| 6   | 23.69                        | 68.49                       | 7.82                          | 1.3778                          |
| 7   | 7.69                         | 81.09                       | 11.22                         | 1.3800                          |
| 8   | 12.10                        | 76.56                       | 11.34                         | 1.3809                          |
| 9   | 2.80                         | 75.59                       | 21.61                         | 1.3831                          |
| 10  | 3.33                         | 66.58                       | 30.09                         | 1.3877                          |
| 11  | 4.32                         | 63.62                       | 32.06                         | 1.3893                          |
| 12  | 5.20                         | 57.05                       | 37.75                         | 1.3928                          |
| 13  | 4.89                         | 52.59                       | 42.52                         | 1.3954                          |
| 14  | 11.45                        | 62.86                       | 25.69                         | 1.3872                          |
| 15  | 20.70                        | 65.58                       | 13.72                         | 1.3808                          |
| 16  | 29.27                        | 59.10                       | 11.63                         | 1.3770                          |
| 17  | 24.63                        | 59.33                       | 16.04                         | 1.3802                          |
| 18  | 29.28                        | 55.90                       | 14.82                         | 1.3781                          |
| 19  | 31.45                        | 52.11                       | 16.44                         | 1.3780                          |

contd.



TABLE 8 CONTD.

| No. | Weight %<br>H <sub>2</sub> O | Weight %<br>HA <sub>c</sub> | Weight T<br>CHCl <sub>3</sub> | n <sub>D</sub> <sup>25.03</sup> |
|-----|------------------------------|-----------------------------|-------------------------------|---------------------------------|
| 20  | 18.18                        | 68.34                       | 13.47                         | 1.3812                          |
| 21  | 18.86                        | 71.91                       | 9.23                          | 1.3793                          |
| 22  | 22.92                        | 66.78                       | 10.29                         | 1.3789                          |
| 23  | 23.04                        | 70.38                       | 6.58                          | 1.3774                          |
| 24  | 2.89                         | 68.01                       | 29.10                         | 1.3870                          |
| 25  | 0.91                         | 18.34                       | 80.75                         | 1.4230                          |
| 26  | 4.22                         | 63.61                       | 32.17                         | 1.3892                          |
| 27  | 3.49                         | 42.19                       | 54.32                         | 1.4023                          |
| 28  | 9.32                         | 65.80                       | 24.88                         | 1.3866                          |
| 29  | 11.78                        | 50.71                       | 37.51                         | 1.3932                          |
| 30  | 10.27                        | 53.37                       | 36.36                         | 1.3926                          |
| 31  | 4.32                         | 73.51                       | 22.17                         | 1.3842                          |
| 32  | 11.56                        | 59.87                       | 28.56                         | 1.3886                          |
| 33  | 8.41                         | 50.88                       | 40.71                         | 1.3950                          |
| 34  | 40.82                        | 48.89                       | 10.29                         | 1.3718                          |
| 35  | 20.57                        | 68.15                       | 11.29                         | 1.3797                          |
| 36  | 24.33                        | 61.11                       | 14.55                         | 1.3798                          |
| 37  | 26.85                        | 64.41                       | 8.74                          | 1.3769                          |
| 38  | 32.09                        | 60.50                       | 7.41                          | 1.3747                          |
| 39  | 49.44                        | 47.45                       | 3.10                          | 1.3653                          |

contd.

TABLE 8 CONTD.

| No. | Weight %<br>H <sub>2</sub> O | Weight %<br>HA <sub>c</sub> | Weight %<br>CHCl <sub>3</sub> | n <sub>D</sub> <sup>25.03</sup> |
|-----|------------------------------|-----------------------------|-------------------------------|---------------------------------|
| 40  | 12.32                        | 59.70                       | 27.98                         | 1.3894                          |
| 41  | 10.75                        | 62.80                       | 26.45                         | 1.3874                          |
| 42  | 16.93                        | 59.96                       | 23.11                         | 1.3852                          |
| 43  | 16.72                        | 50.26                       | 33.02                         | 1.3898                          |
| 44  | 24.21                        | 51.73                       | 24.06                         | 1.3841                          |
| 45  | 9.11                         | 63.43                       | 27.46                         | 1.3879                          |
| 46  | 15.54                        | 75.77                       | 8.69                          | 1.3794                          |
| 47  | 25.21                        | 51.23                       | 23.56                         | 1.3831                          |
| 48  | 3.14                         | 61.43                       | 35.43                         | 1.3907                          |
| 49  | 16.67                        | 69.31                       | 14.02                         | 1.3814                          |
| 50  | 14.42                        | 63.90                       | 21.68                         | 1.3850                          |
| 51  | 28.99                        | 52.89                       | 18.12                         | 1.3794                          |
| 52  | 6.65                         | 73.86                       | 19.49                         | 1.3833                          |
| 53  | 12.69                        | 74.32                       | 12.99                         | 1.3814                          |
| 54  | 14.37                        | 65.14                       | 20.49                         | 1.3844                          |
| 55  | 9.85                         | 85.06                       | 5.09                          | 1.3778                          |
| 56  | 19.86                        | 60.08                       | 20.06                         | 1.3831                          |
| 57  | 8.70                         | 71.00                       | 20.31                         | 1.3842                          |
| 58  | 6.65                         | 66.86                       | 26.49                         | 1.3870                          |
| 59  | 16.89                        | 51.37                       | 31.74                         | 1.3892                          |

contd.

TABLE 8 CONTD.

| No. | Weight %<br>H <sub>2</sub> O | Weight %<br>HA <sub>c</sub> | Weight %<br>CHCl <sub>3</sub> | n <sub>D</sub> <sup>25.03</sup> |
|-----|------------------------------|-----------------------------|-------------------------------|---------------------------------|
| 60  | 15.34                        | 77.21                       | 7.45                          | 1.3789                          |
| 61  | 13.47                        | 51.99                       | 34.54                         | 1.3913                          |
| 62  | 5.29                         | 48.01                       | 46.69                         | 1.3980                          |
| 63  | 7.33                         | 61.54                       | 31.13                         | 1.3898                          |
| 64  | 8.67                         | 44.29                       | 47.05                         | 1.3987                          |
| 65  | 8.19                         | 62.14                       | 29.66                         | 1.3889                          |
| 66  | 8.40                         | 58.30                       | 33.30                         | 1.3909                          |

C. VAPOUR-LIQUID EQUILIBRIA(1) THE SYSTEM WATER-ACETIC ACID

The results of the pressure measurements are reported in Table 9. Here the total pressure is given versus the concentration of the acetic acid in the liquid phase expressed in percentage by weight. See also Figure 9.

In Table 10 the results of the isothermal distillations are reported, giving the equilibrium liquid and vapour compositions expressed in percentage acetic acid by weight. The results are also plotted graphically as in Figure 10.

The data of Table 9 have been treated according to the Gibbs formula as has been discussed on page 16. The vapour compositions corresponding to the liquid compositions are found graphically from Figure 10. In Table 11 the final results of the dimerization calculations are represented. This Table gives respectively: the composition of the liquid in weight percentage and in mole percentage, the latter being based on the average molecular weight of the acetic acid in the vapour phase. The composition of the coexisting vapour is reported in weight and mole percentage as well as the average molecular weight of the acetic acid in the vapour phase, the percentage dimer

of acetic acid in the vapour phase, the total vapour pressure, the partial vapour pressures of water and acetic acid, the part of the partial vapour pressure of the acetic acid due to the dimers ( $p^{11}$ ) and to the monomers ( $p^1$ ) and finally the dimerization constant as defined by equation (27) on page 17. The results obtained are plotted in Figure 11, which shows the dependence of the total and partial vapour pressures upon the concentration of the acetic acid in mole fraction.

The data as reported in Table 11 have been treated according to the formulae (18) as proposed by von Zawidzki<sup>9</sup>. After making use of approximations and of smoothed total pressure data the constants  $\frac{\alpha_2}{2} = 0.41$  and  $\frac{\alpha_3}{3} = -0.30$  are obtained for acetic acid, so that according to (18) there follows for water  $\frac{\beta_2}{2} = -0.04$  and  $\frac{\beta_3}{3} = +0.30$ . The final results are reported in Table 12, showing the partial pressures as measured against the partial pressures as calculated.

#### The Function f(y)

The data reported in Table 11 have been used to calculate the  $f(y)$  as defined in equation (21). The relative volatility as reported in equation (23) has also been calculated. The quantity  $\frac{P_2^0}{P_1^0} \alpha = 0.664 \alpha$  is

tabulated. The results are reported in Table 13. In Figure 12  $f(y)$  is given as a function of the mole fraction of the water in the vapour phase ( $y$ ). The ideal curve  $f_{id}(y)$  is calculated according to the formula

$$f_{id}(y) = - \frac{1}{a - y} \quad (32)$$

$$\text{where } a = \frac{p_1^{\circ}}{p_1^{\circ} - p_2^{\circ}} = \frac{23.8}{23.8 - 15.8} = 2.98$$

Therefore  $f_{id}(y) = - \frac{1}{(2.98 - y)}$ . In Figure 13 a plot of the function  $0.664 \alpha$  as a function of  $y$  is given.

TABLE 9TOTAL VAPOUR PRESSURES IN THE SYSTEMWATER-ACETIC ACIDAT 25°C

| Liquid<br>Weight % HA <sub>c</sub> | P<br>mm Hg |
|------------------------------------|------------|
| 100.0                              | 15.7       |
| 97.8                               | 18.1       |
| 95.0                               | 19.3       |
| 80.8                               | 21.2       |
| 69.1                               | 21.9       |
| 57.3                               | 22.7       |
| 33.2                               | 23.5       |
| 27.6                               | 23.6       |
| 18.9                               | 23.8       |
| 0.0                                | 23.8       |

LEGEND TO FIGURE 9

The Total Vapour Pressure as a Function of  
the Concentration by Weight in the  
System Acetic Acid-Water at 25°C



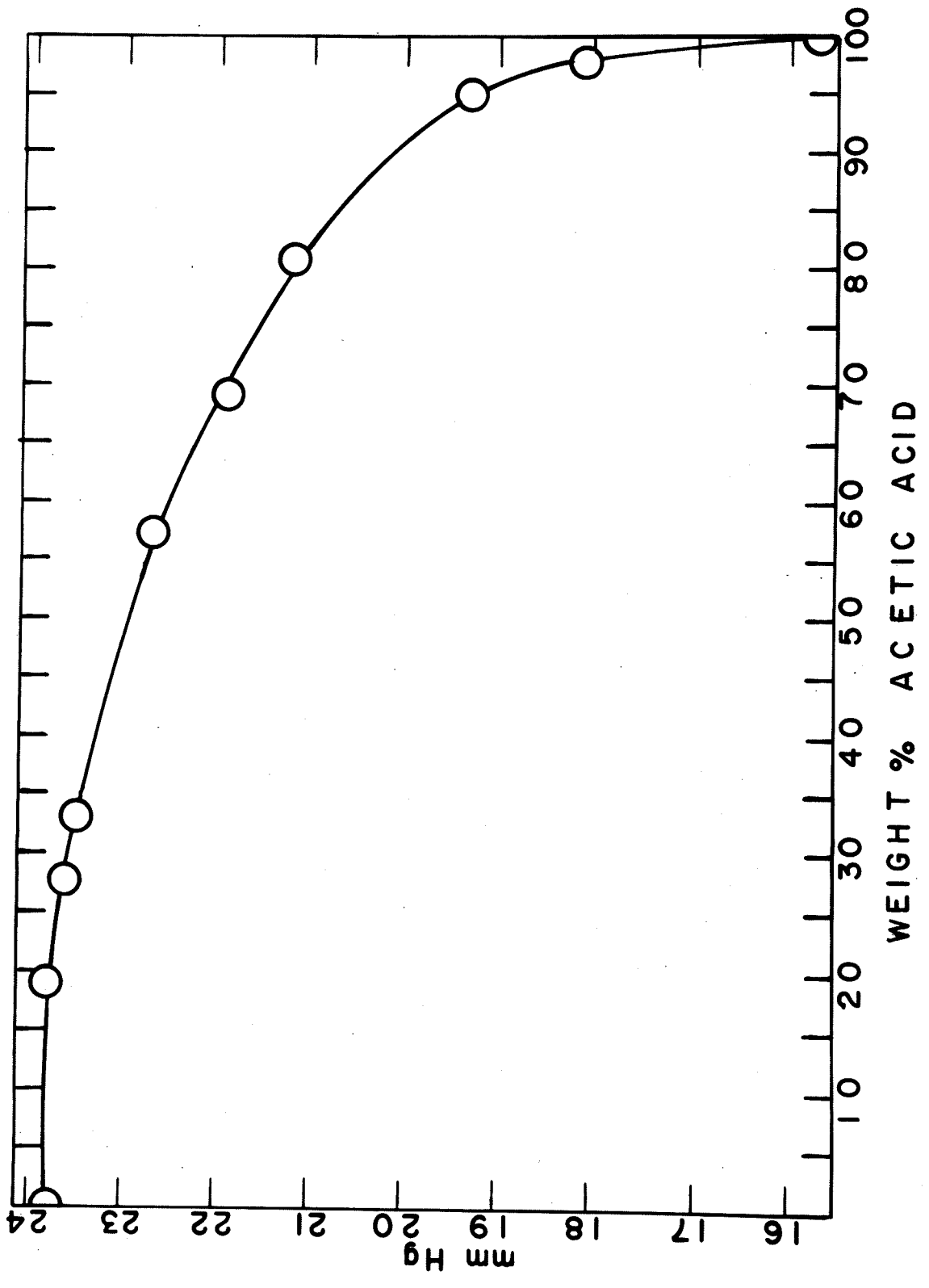


TABLE 10  
VAPOUR-LIQUID EQUILIBRIUM COMPOSITIONS  
OF THE SYSTEM WATER-ACETIC ACID  
AT 25°C

| Liquid<br>Weight % HA <sub>c</sub> | Vapour<br>Weight % HA <sub>c</sub> |
|------------------------------------|------------------------------------|
| 55.2                               | 47.4                               |
| 25.2                               | 17.9                               |
| 57.8                               | 50.0                               |
| 73.4                               | 66.1                               |
| 85.3                               | 79.2                               |
| 95.6                               | 89.6                               |
| 81.6                               | 76.0                               |
| 88.7                               | 82.8                               |
| 91.1                               | 86.7                               |
| 98.3                               | 96.0                               |
| 94.4                               | 90.1                               |
| 18.3                               | 12.4                               |

LEGEND TO FIGURE 10

Liquid-Vapour Composition Equilibrium Curve

For the System Acetic Acid-Water at 25°C

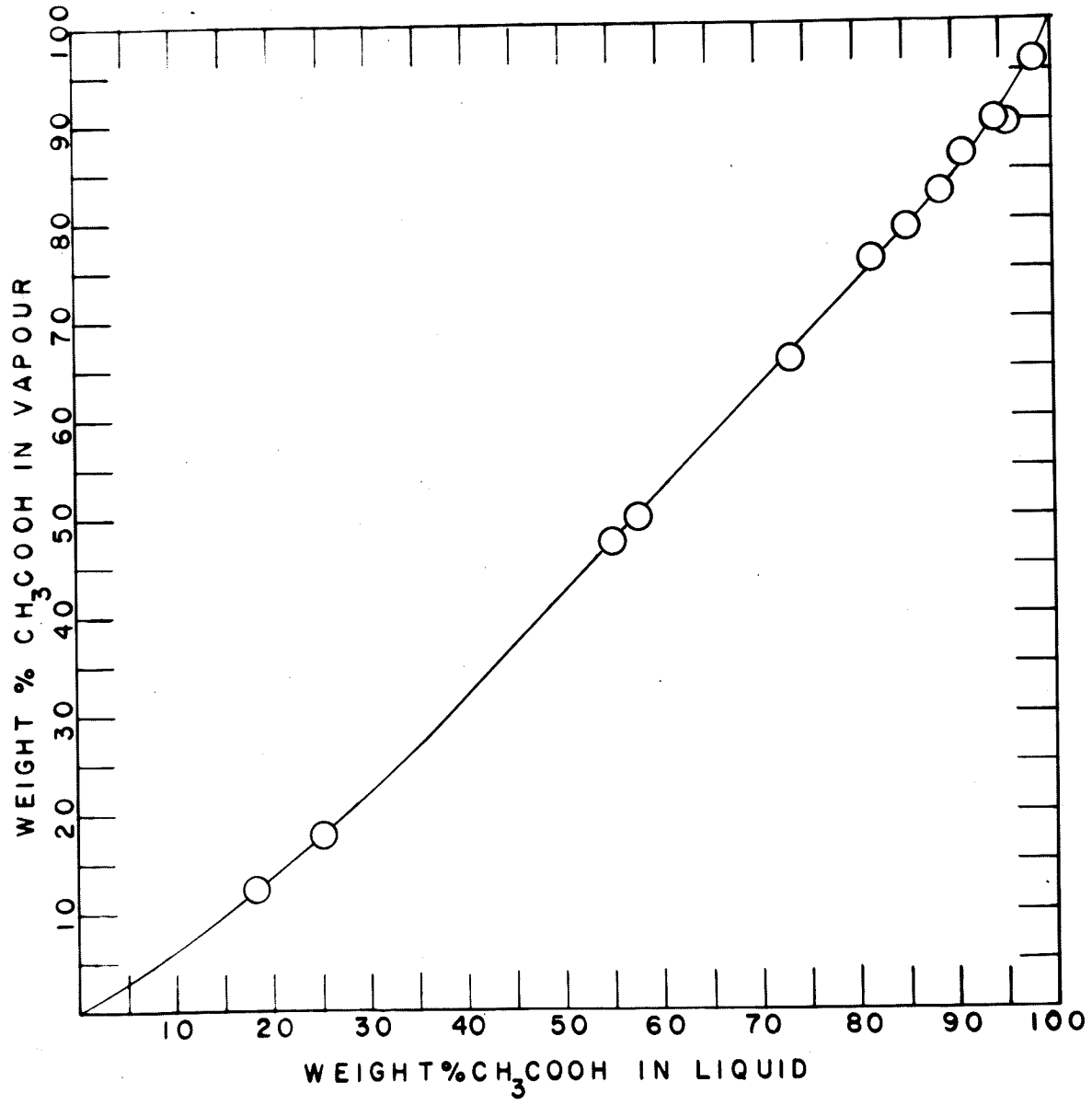


TABLE 11DIMERIZATION DATA FOR THE SYSTEM WATER-ACETIC ACID

| No. | Liquid                |                        | Vapour                |                        | M     | %<br>dimer |
|-----|-----------------------|------------------------|-----------------------|------------------------|-------|------------|
|     | Wt. % HA <sub>c</sub> | Mole % HA <sub>c</sub> | Wt. % HA <sub>c</sub> | Mole % HA <sub>c</sub> |       |            |
| 1   | 100.0                 | 100.0                  | 100.0                 | 100.0                  |       |            |
| 2   | 97.8                  | 87.6                   | 95.5                  | 77.4                   | 111.4 | 85.5       |
| 3   | 95.0                  | 75.4                   | 90.9                  | 61.9                   | 110.7 | 84.3       |
| 4   | 80.8                  | 41.3                   | 74.5                  | 32.7                   | 108.1 | 80.1       |
| 5   | 69.1                  | 27.9                   | 62.2                  | 22.1                   | 104.2 | 73.6       |
| 6   | 57.3                  | 18.9                   | 49.9                  | 14.7                   | 103.6 | 72.6       |
| 7   | 33.2                  | 8.4                    | 25.4                  | 5.9                    | 97.1  | 61.8       |
| 8   | 27.6                  | 6.8                    | 20.2                  | 4.6                    | 94.6  | 57.6       |
| 9   | 18.9                  | 4.4                    | 12.8                  | 2.9                    | 90.2  | 50.3       |

Contd.

TABLE 11 CONTD.

| No. | $P_{total}^*$ | $P_{H_2O}$ | $P_{HA_c}$ | $P''$ | $P'$ | K    |
|-----|---------------|------------|------------|-------|------|------|
| 1   | 15.7          | -          | 15.7       | -     | -    | 2.89 |
| 2   | 18.1          | 4.1        | 14.0       | 12.0  | 2.0  | 3.00 |
| 3   | 19.3          | 7.3        | 12.0       | 10.1  | 1.9  | 2.81 |
| 4   | 21.2          | 14.3       | 6.9        | 5.5   | 1.4  | 2.81 |
| 5   | 21.9          | 17.0       | 4.9        | 3.6   | 1.3  | 2.13 |
| 6   | 22.7          | 19.4       | 3.3        | 2.4   | 0.9  | 2.96 |
| 7   | 23.5          | 22.1       | 1.4        | 0.85  | 0.55 | 2.83 |
| 8   | 23.6          | 22.5       | 1.1        | 0.6   | 0.5  | 2.40 |
| 9   | 23.8          | 23.1       | 0.7        | 0.35  | 0.35 | 2.86 |

\* Pressures in mm Hg

Average K = 2.8

LEGEND TO FIGURE 11

Total and Partial Vapour Pressure

Curves on a Dimerized Basis

For the System Acetic Acid-Water at 25°C

CD Total pressure curves<sup>\*</sup>

AD Partial pressures of acetic acid

BC Partial pressures of water

<sup>\*</sup> The straight lines are the "ideal" curves

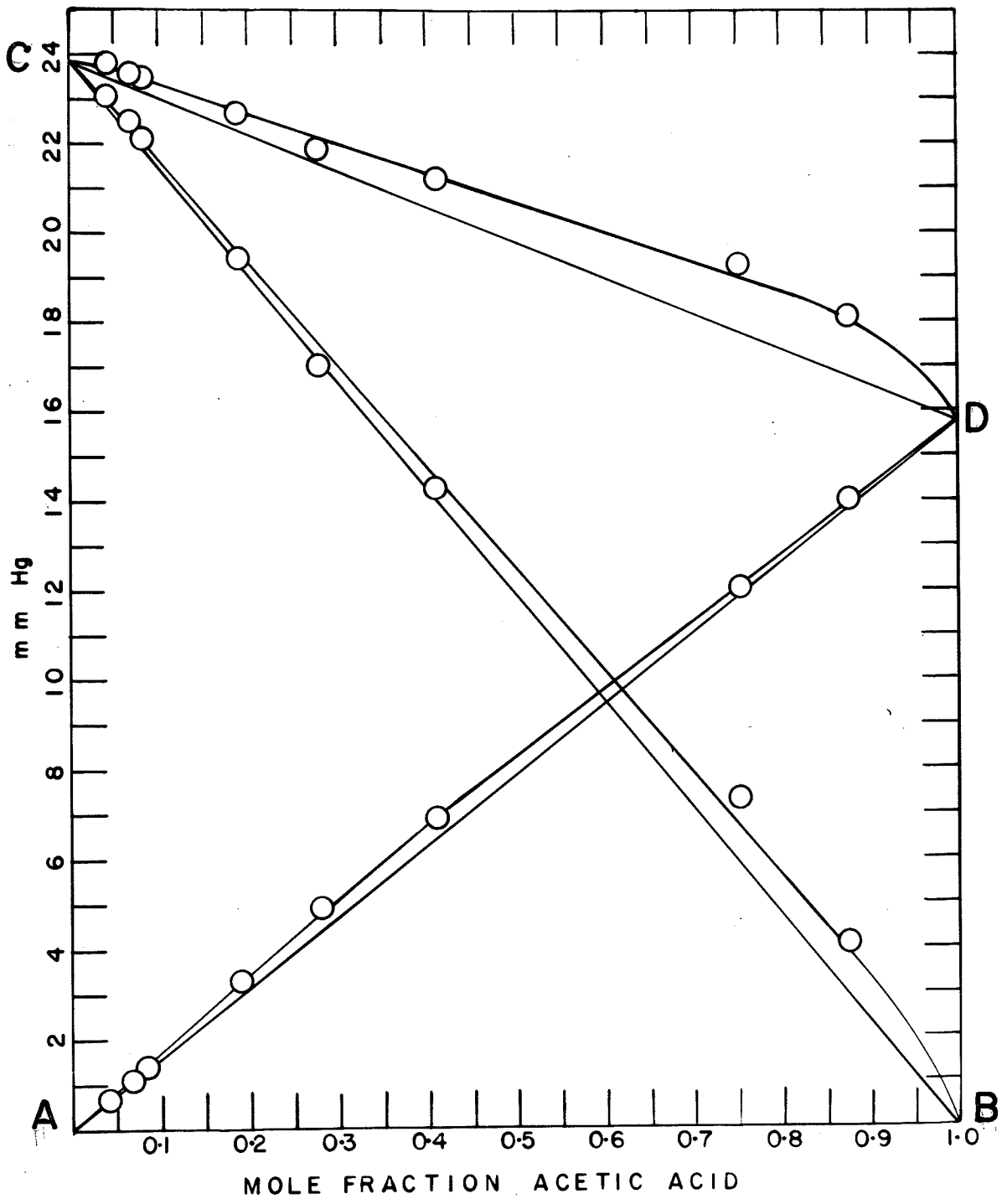




TABLE 12PARTIAL PRESSURES OBTAINED WITH VON ZAWIDZKITREATMENT IN THE SYSTEMWATER-ACETIC ACID AT 25°C

| No. | Acetic Acid |         | Water      |         |
|-----|-------------|---------|------------|---------|
|     | P measured  | P calc. | P measured | P calc. |
| 1   | 15.7        | 15.8    | 0          | 0       |
| 2   | 14.0        | 13.9    | 4.1        | 3.6     |
| 3   | 12.0        | 12.2    | 7.3        | 6.6     |
| 4   | 6.9         | 7.1     | 14.3       | 14.2    |
| 5   | 4.9         | 4.9     | 17.0       | 17.2    |
| 6   | 3.3         | 3.3     | 19.4       | 19.3    |
| 7   | 1.4         | 1.5     | 22.1       | 22.0    |
| 8   | 1.1         | 1.2     | 22.5       | 22.2    |
| 9   | 0.7         | 0.8     | 23.1       | 22.8    |

TABLE 13

F(y) AND RELATIVE VOLATILITY DATA FOR  
THE SYSTEM WATER-ACETIC ACID AT 25°C

| x <sup>*</sup> | y     | f(y)<br>negative | 0.664. $\alpha$ |
|----------------|-------|------------------|-----------------|
| 0.124          | 0.226 | 0.583            | 1.370           |
| 0.246          | 0.381 | 0.572            | 1.253           |
| 0.587          | 0.673 | 0.391            | 0.961           |
| 0.721          | 0.779 | 0.337            | 0.906           |
| 0.811          | 0.853 | 0.336            | 0.898           |
| 0.916          | 0.941 | 0.450            | 0.971           |
| 0.932          | 0.954 | 0.729            | 1.005           |
| 0.956          | 0.971 | 0.541            | 1.023           |

\* x = mole fraction H<sub>2</sub>O in liquid

y = mole fraction H<sub>2</sub>O in vapour

LEGEND TO FIGURE 12

F(y) For the System Acetic Acid-Water

At 25°C

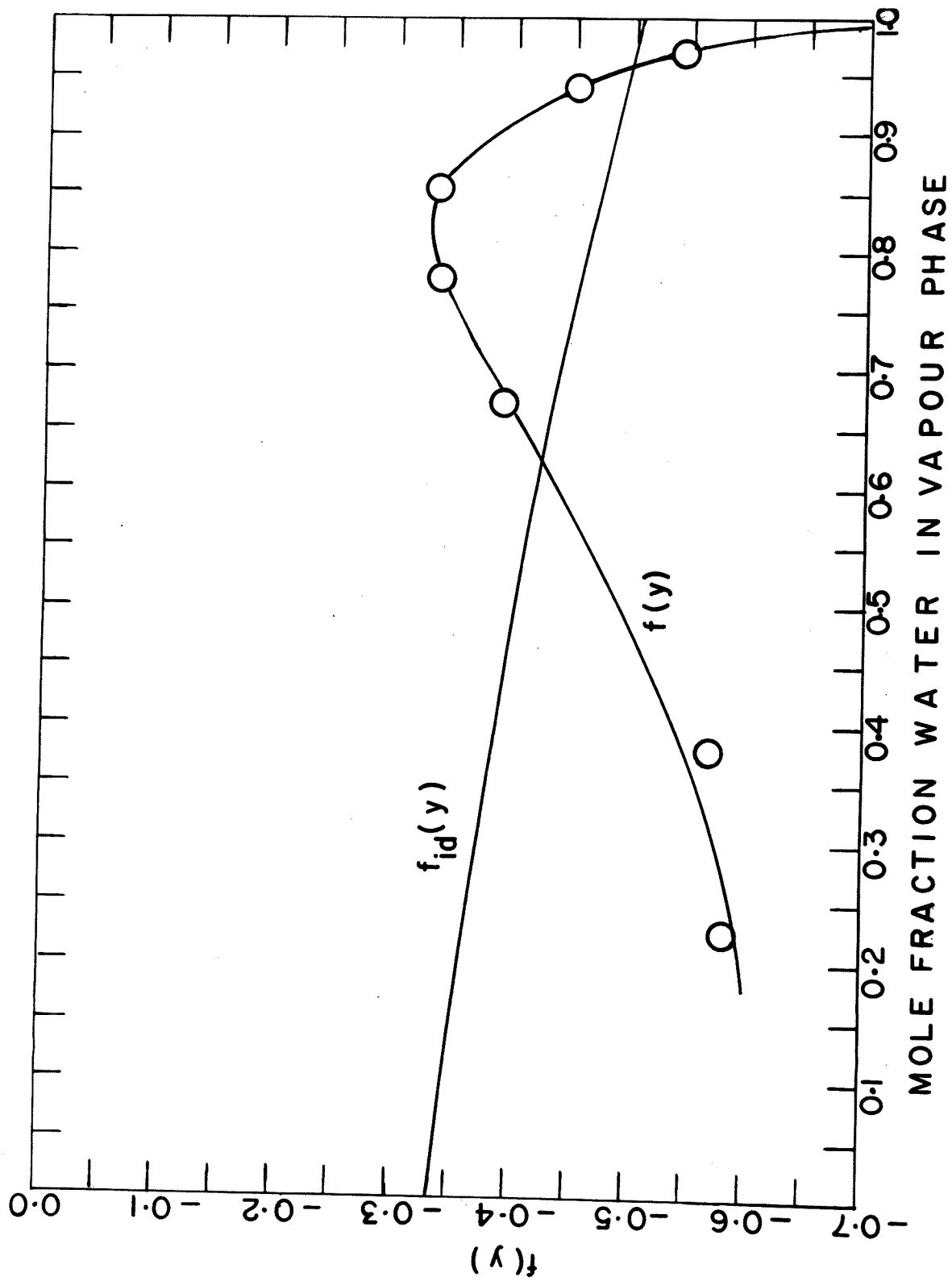
LEGEND TO FIGURE 13

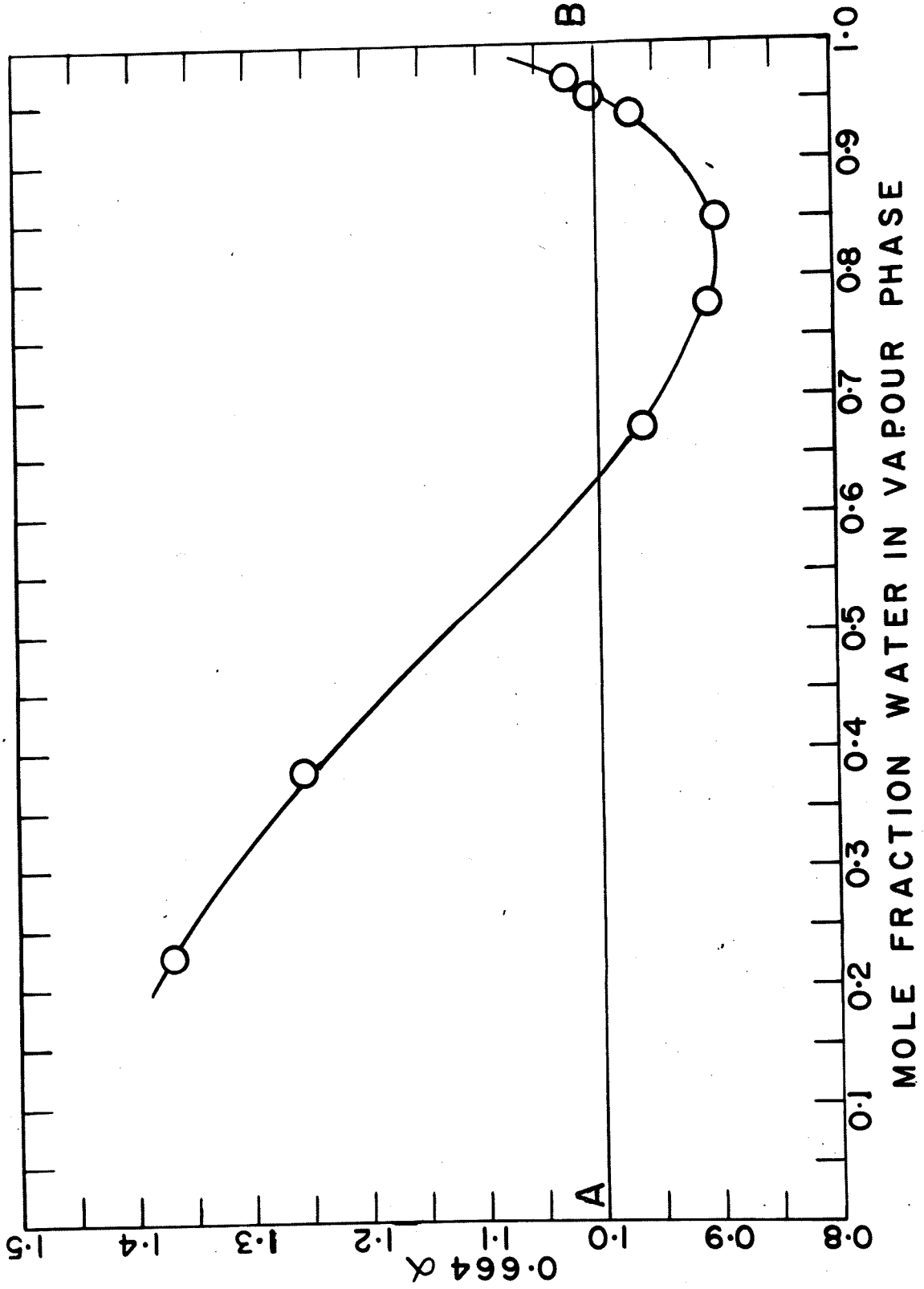
The Relative Volatility Function

in the System Acetic Acid-Water

At 25°C

AB Ideal behaviour





(2) THE SYSTEM CHLOROFORM-ACETIC ACID

The results of the pressure measurements are reported in Table 14. The results are also graphically represented in Figure 14.

The results of the determinations of the compositions of the vapour that is in equilibrium with a liquid of a certain concentration are reported in Table 15. The figures in brackets are the number of determinations from which the average is obtained. The results are represented graphically in Figure 15.

The data of Table 14 have been treated for dimerization of the acetic acid in the vapour phase in a similar way as in the system water-acetic acid. The results are reported in Table 16. In Figure 16 the total and partial vapour pressures are represented as a function of the liquid composition expressed in the mole fraction of chloroform. The calculation of the mole fraction is again based on the average molecular weight of the acetic acid in the vapour phase.

The data of Table 16 are again treated according to the formulae (18). Using smoothed data for chloroform the constants  $\frac{\alpha_2}{2} = 0.155$  and  $\frac{\alpha_3}{3} = -0.16$  are obtained. This gives for acetic acid the constants

$\beta_2 = -0.085$  and  $\beta_3 = +0.16$ . The final results

are reported in Table 17.

The function  $f(y)$

The data reported in Table 16 have been used to calculate the  $f(y)$ . The relative volatility has also been calculated. This quantity is tabulated in the form

of  $\frac{p_2^0}{p_1^0} \alpha = 0.0794 \alpha$ . The results are reported in

Table 18. In Figure 17 the  $f(y)$  is given as a function of the vapour phase mole fraction of chloroform. In Figure 18 is represented the curve for  $0.0794 \alpha$  as a function of the vapour phase mole fraction of chloroform.

TABLE 14TOTAL VAPOUR PRESSURES IN THE SYSTEMACETIC ACID-CHLOROFORM

| Liquid.<br>Weight % $\text{CHCl}_3$ | P<br>mm Hg |
|-------------------------------------|------------|
| 15.6                                | 46.4       |
| 19.2                                | 51.3       |
| 23.5                                | 58.6       |
| 34.3                                | 77.4       |
| 43.8                                | 93.5       |
| 47.6                                | 101.7      |
| 68.8                                | 141.1      |
| 85.4                                | 173.5      |



LEGEND TO FIGURE 14

The Total Pressure as a Function of  
The Composition Expressed in Weight Percent  
In the system Acetic Acid-Chloroform at 25°C

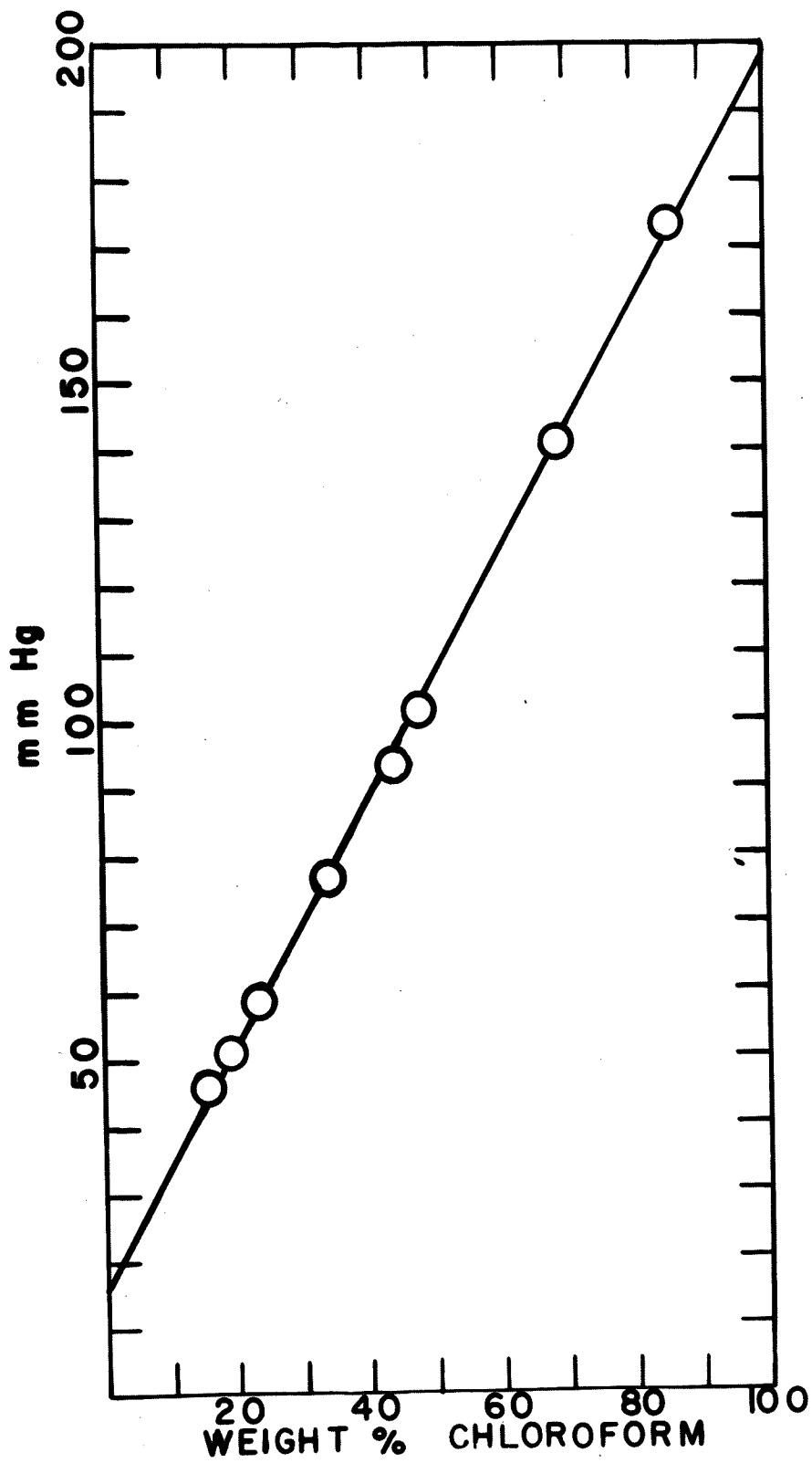


TABLE 15VAPOUR-LIQUID EQUILIBRIUM COMPOSITIONSOF THE SYSTEM ACETIC ACID-CHLOROFORMAT 25°C

| Liquid<br>Weight % $\text{CHCl}_3$ | Vapour<br>Weight % $\text{CHCl}_3$ |
|------------------------------------|------------------------------------|
| 9.3 (2)                            | 56.3                               |
| 25.8 (3)                           | 81.4                               |
| 30.1 (1)                           | 85.4                               |
| 32.5 (3)                           | 88.2                               |
| 41.6 (3)                           | 89.7                               |
| 53.1 (4)                           | 93.2                               |
| 61.9 (1)                           | 94.4                               |

LEGEND TO FIGURE 15

Liquid-Vapour Equilibrium Composition Curve

For the System Acetic Acid-Chloroform

At 25°C

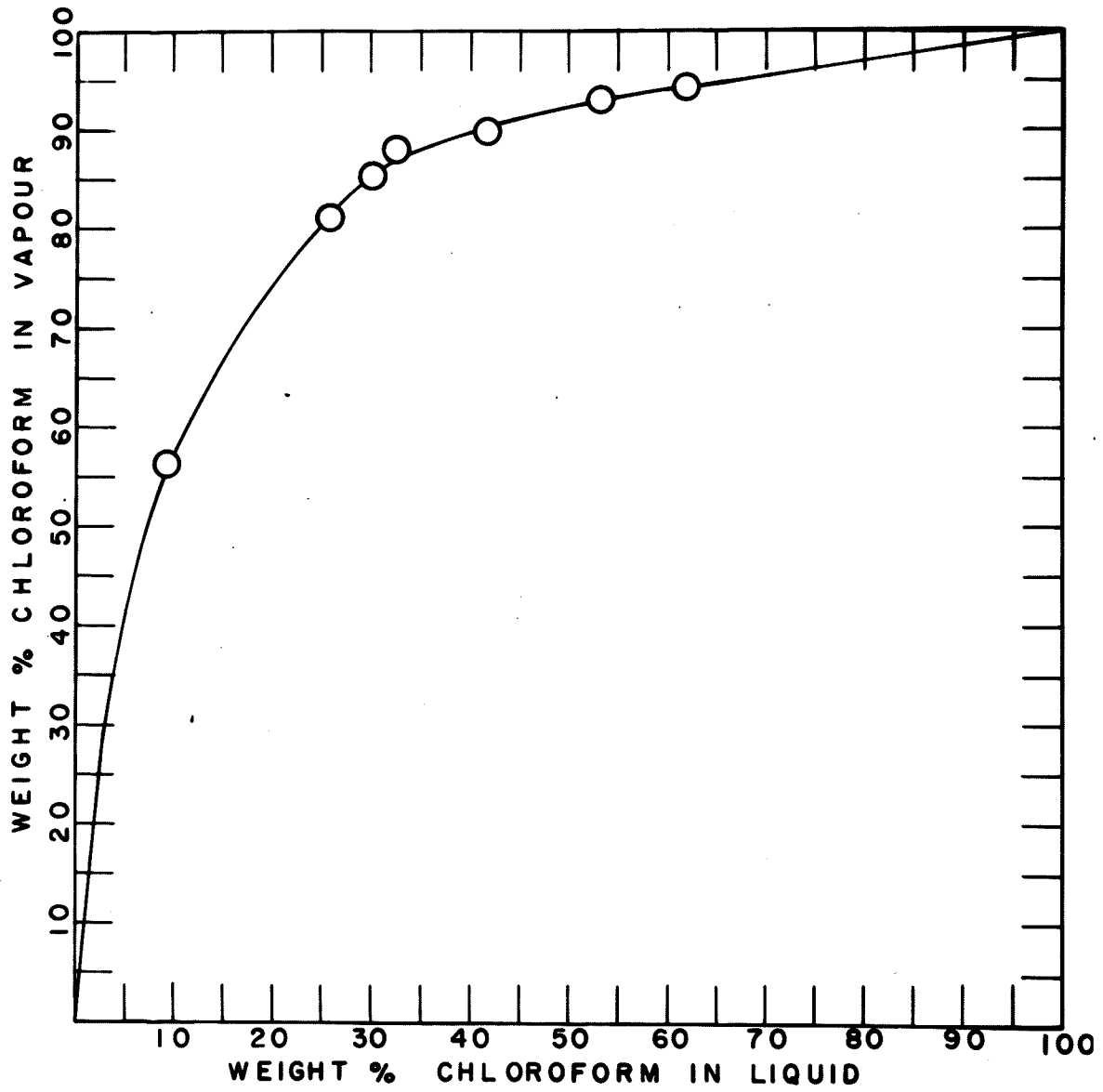


TABLE 16

DIMERIZATION DATA FOR THE SYSTEMACETIC ACID-CHLOROFORM

| No. | Liquid               |                        | Vapour               |                        | M     | %<br>dimer |
|-----|----------------------|------------------------|----------------------|------------------------|-------|------------|
|     | Wt.% $\text{CHCl}_3$ | Mole % $\text{CHCl}_3$ | Wt.% $\text{CHCl}_3$ | Mole % $\text{CHCl}_3$ |       |            |
| 1   | 0.0                  | 0.0                    | 0.0                  | 0.0                    | -     | -          |
| 2   | 15.6                 | 14.8                   | 68.6                 | 67.2                   | 111.7 | 86.0       |
| 3   | 19.2                 | 18.2                   | 73.9                 | 72.5                   | 111.2 | 85.2       |
| 4   | 23.5                 | 22.2                   | 79.0                 | 77.8                   | 111.1 | 85.0       |
| 5   | 34.3                 | 32.5                   | 87.1                 | 86.2                   | 110.3 | 83.6       |
| 6   | 43.8                 | 41.7                   | 90.5                 | 89.8                   | 109.7 | 82.8       |
| 7   | 47.6                 | 45.5                   | 91.6                 | 90.9                   | 109.6 | 82.5       |
| 8   | 68.8                 | 66.4                   | 96.2                 | 95.8                   | 107.3 | 78.7       |
| 9   | 85.4                 | 83.5                   | 98.5                 | 98.3                   | 103.0 | 71.6       |
| 10  | 100.0                | 100.0                  | 100.0                | 100.0                  | -     |            |

Contd.

TABLE 16 CONTD.

| No. | P <sup>*</sup><br>total | P<br>CHCl <sub>3</sub> | P<br>HA <sub>c</sub> | P''  | P'  | K    |
|-----|-------------------------|------------------------|----------------------|------|-----|------|
| 1   | 15.8                    | 0.0                    | 15.8                 |      |     | 2.89 |
| 2   | 46.4                    | 31.2                   | 15.2                 | 13.1 | 2.1 | 2.97 |
| 3   | 51.3                    | 37.2                   | 14.1                 | 12.0 | 2.1 | 2.72 |
| 4   | 58.6                    | 45.6                   | 13.0                 | 11.0 | 2.0 | 2.75 |
| 5   | 77.4                    | 66.7                   | 10.7                 | 8.9  | 1.8 | 2.75 |
| 6   | 93.5                    | 83.9                   | 9.6                  | 7.9  | 1.7 | 2.75 |
| 7   | 101.7                   | 92.5                   | 9.2                  | 7.6  | 1.6 | 2.91 |
| 8   | 141.1                   | 135.2                  | 5.9                  | 4.7  | 1.3 | 2.78 |
| 9   | 173.5                   | 170.5                  | 3.0                  | 2.2  | 0.9 | 2.72 |
| 10  | 199.1                   | 199.1                  | 0.0                  | -    | -   | -    |

\* Pressures in mm Hg

Average K = 2.75

LEGEND TO FIGURE 16

Total and Partial Vapour Pressure Curves

On a Dimerised Basis For the System

Acetic Acid-Chloroform at 25°C

CD Total pressure curves.\*

AD Partial pressures of chloroform

BC Partial pressures of acetic acid

\* The straight lines are the "ideal" curves



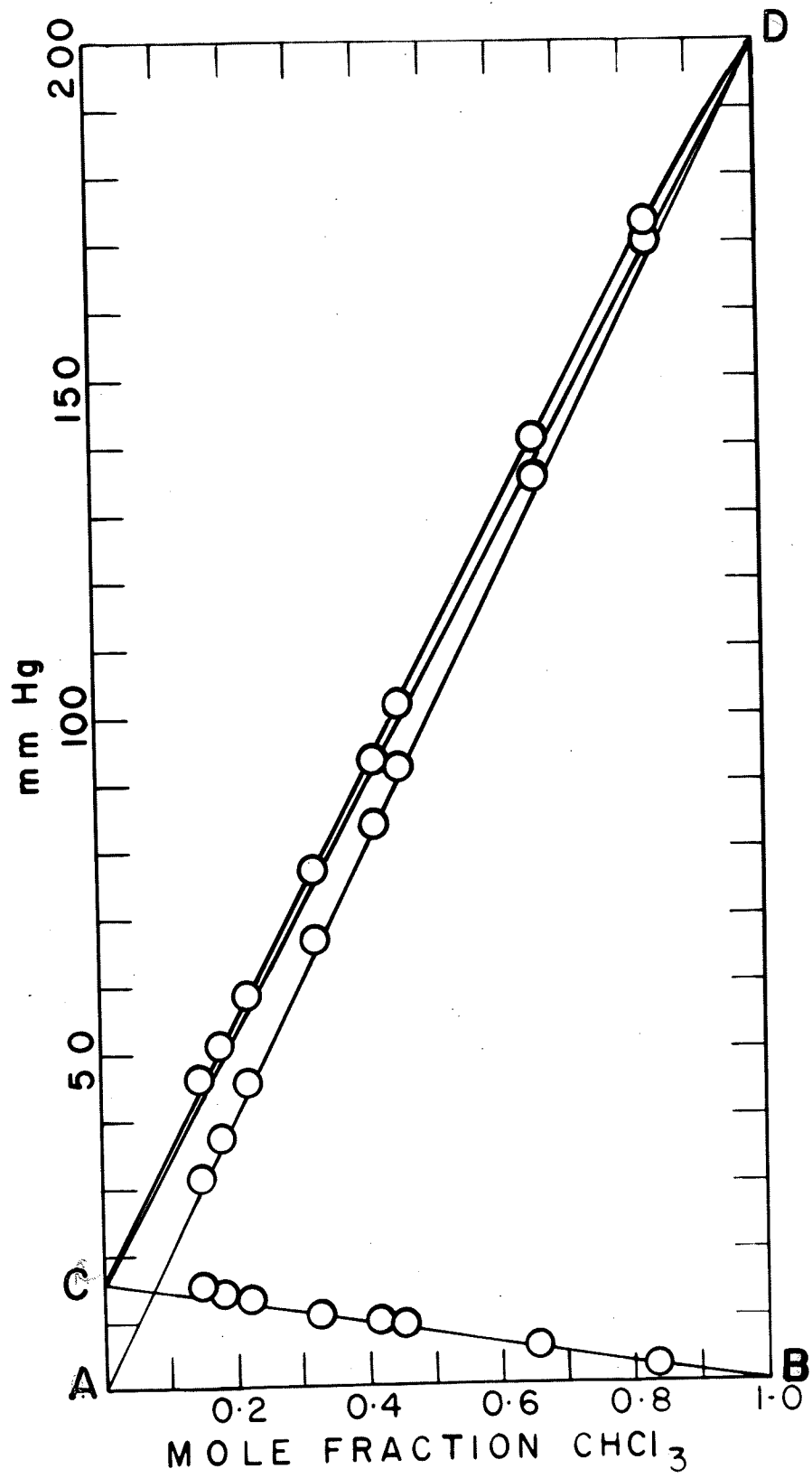


TABLE 17

PARTIAL PRESSURES OBTAINED WITH  
VON ZAWIDZKI TREATMENT IN THE SYSTEM  
ACETIC ACID-CHLOROFORM

| No. | Chloroform         |                     |                    | Acetic Acid        |                     |                    |
|-----|--------------------|---------------------|--------------------|--------------------|---------------------|--------------------|
|     | P <sub>meas.</sub> | P <sub>smooth</sub> | P <sub>calc.</sub> | P <sub>meas.</sub> | P <sub>smooth</sub> | P <sub>calc.</sub> |
| 2   | 31.2               | 29.8                | 29.8               | 15.2               | 14.5                | 13.4               |
| 3   | 37.2               | 36.7                | 36.7               | 14.1               | 13.9                | 12.9               |
| 4   | 45.6               | 45.0                | 45.0               | 13.0               | 12.9                | 12.3               |
| 5   | 66.7               | 66.7                | 66.2               | 10.7               | 10.7                | 10.6               |
| 6   | 83.9               | 84.6                | 84.9               | 9.6                | 9.7                 | 9.2                |
| 7   | 92.5               | 92.5                | 92.5               | 9.2                | 9.2                 | 8.4                |
| 8   | 135.2              | 135.0               | 134.0              | 5.9                | 5.9                 | 5.4                |
| 9   | 170.5              | 170.0               | 167.0              | 3.0                | 2.5                 | 2.7                |

TABLE 18

f(y) AND RELATIVE VOLATILITY DATA FOR  
THE SYSTEM ACETIC ACID-CHLOROFORM

| $x$ * | $y$   | $f(y)$<br>negative | 0.079. |
|-------|-------|--------------------|--------|
| 0.148 | 0.672 | 2.375              | 1.062  |
| 0.182 | 0.725 | 2.371              | 0.941  |
| 0.222 | 0.778 | 3.214              | 0.975  |
| 0.325 | 0.862 | 4.505              | 1.030  |
| 0.417 | 0.898 | 5.004              | 0.977  |
| 0.455 | 0.909 | 5.506              | 0.950  |
| 0.664 | 0.958 | 7.280              | 0.916  |
| 0.835 | 0.983 | 8.657              | 0.907  |

$x$  = mole fraction  $\text{CHCl}_3$  in liquid

$y$  = mole fraction  $\text{CHCl}_3$  in vapour

LEGEND TO FIGURE 17

F(y) For the System Acetic Acid-Chloroform

At 25°C

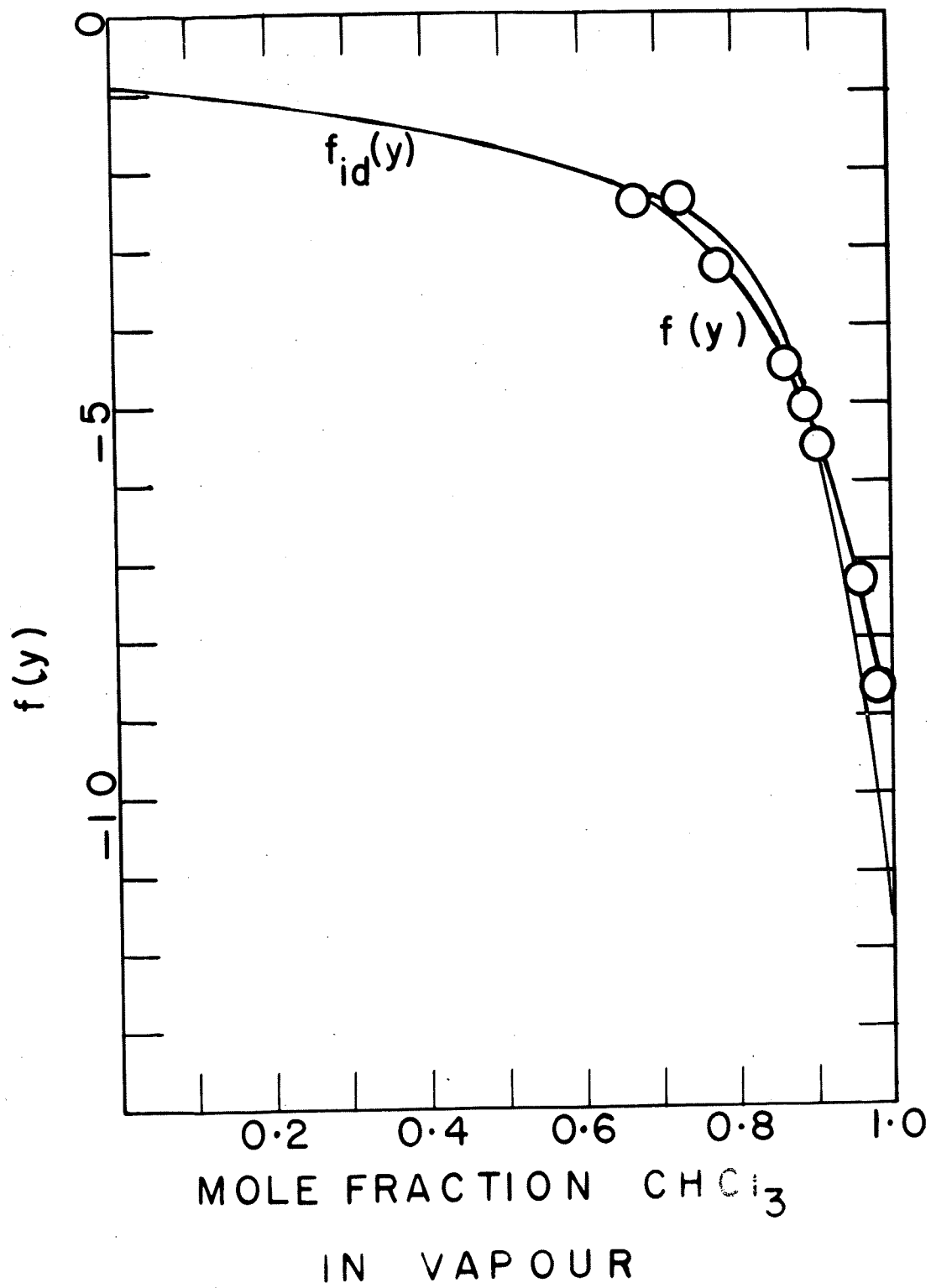
LEGEND TO FIGURE 18

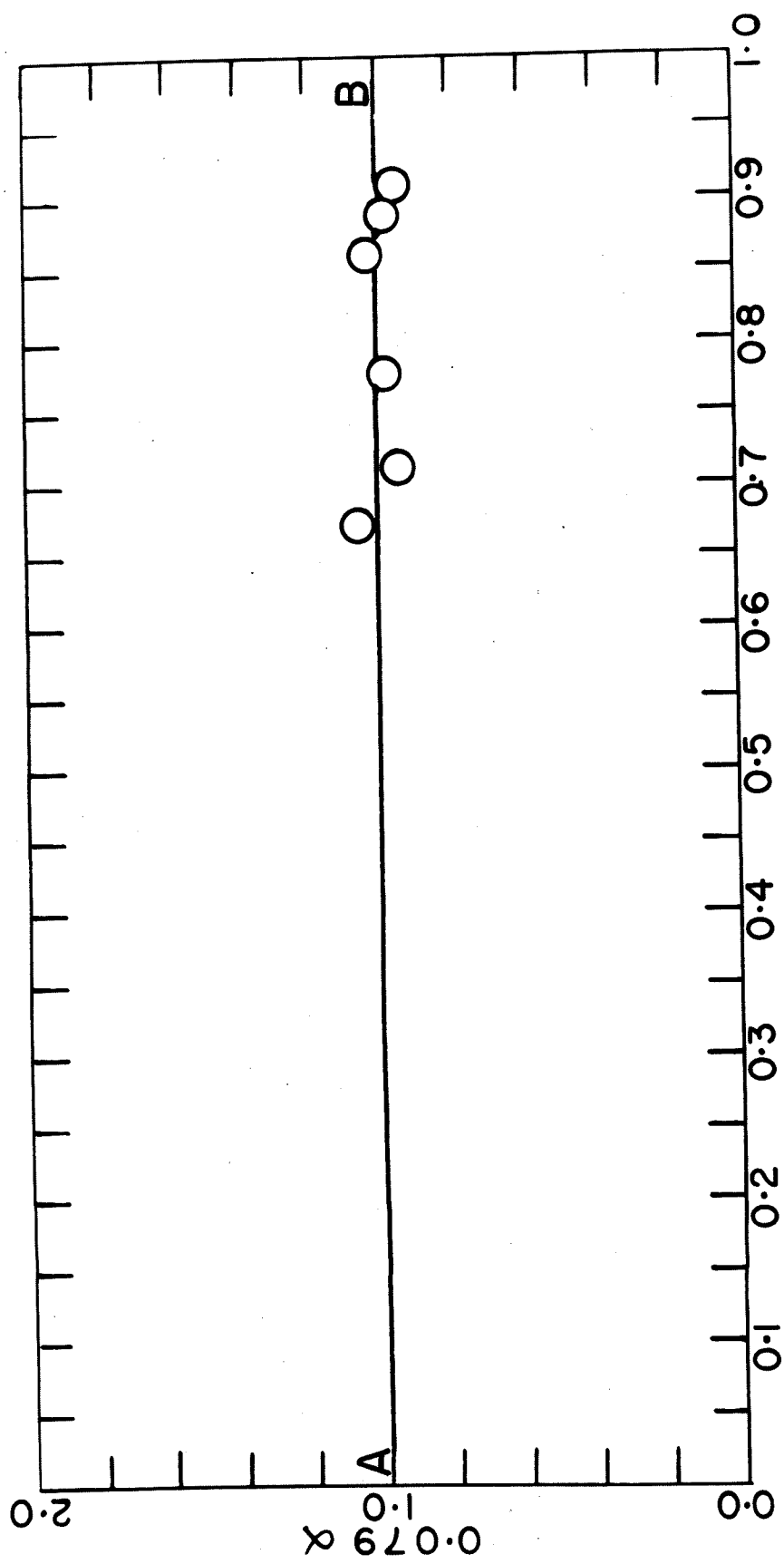
The Relative Volatility Function For

The System Acetic Acid-Chloroform

At 25°C

AB Ideal behaviour





MOLE FRACTION CHLOROFORM IN VAPOUR

(3) THE SYSTEM ACETIC ACID-CHLOROFORM-WATER

The total vapour pressures in dependence on the composition of the liquid phase are reported in Table 19. The compositions are also represented in Figure 19 by means of the circles.

The results of the determinations of the composition of the vapour phase that is in equilibrium with a liquid of a certain composition are reported in Table 20. The figures in brackets indicate the number of determinations from which the average is taken. The liquid compositions are presented in Figure 19 by means of the black circles. In the last column of Table 20 the corresponding vapour pressures, which are interpolated from the data of Table 19, are presented. The accuracy of these data is  $\pm^3$  mm, but for No. 4 the accuracy is much larger. This is because the liquid composition of No. 5 in Table 19 is virtually identical to the liquid composition of No. 4 in Table.20.

In Table 21 the dimerization data are represented. The mole fractions are again calculated on a dimerized basis.

TABLE 19TOTAL VAPOUR PRESSURES IN THE SYSTEMACETIC ACID-CHLOROFORM-WATER AT 25°C

| No.    | Liquid Composition |                   |                  | Pressure<br>mm Hg |
|--------|--------------------|-------------------|------------------|-------------------|
|        | HA <sub>c</sub>    | CHCl <sub>3</sub> | H <sub>2</sub> O |                   |
| 1      | 67.7               | 21.9              | 10.4             | 94.7              |
| 2      | 53.0               | 39.3              | 7.7              | 145.7             |
| 3      | 58.8               | 32.0              | 9.2              | 129.3             |
| 4      | 60.4               | 12.6              | 27.0             | 129.9             |
| 5      | 65.8               | 4.3               | 29.9             | 73.6              |
| 6      | 61.9               | 20.0              | 18.1             | 121.6             |
| 7      | 43.4               | 44.6              | 12.0             | 171.3             |
| 8      | 49.0               | 36.9              | 14.1             | 161.6             |
| 9      | 74.1               | 16.2              | 9.7              | 76.3              |
| 10     | 71.4               | 20.2              | 8.4              | 85.5              |
| 11     | -                  | (50)              | (50)             | 210.5             |
| 12 (a) | 28.9               | 1.5               | 69.6             | 167.5             |
| (b)    | 8.2                | 90.6              | 1.2              |                   |



TABLE 20

VAPOUR-LIQUID EQUILIBRIUM COMPOSITIONS  
IN THE SYSTEM ACETIC ACID-CHLOROFORM-WATER  
AT 25°C

| No. | Liquid Composition  | Vapour Composition   | Total Pressure <sup>*</sup> |
|-----|---|--|-----------------------------|
| 1   | 55.0 % HA <sub>c</sub><br>28.6 % CHCl <sub>3</sub> (2)<br>16.4 % H <sub>2</sub> O | 3.5 % HA <sub>c</sub><br>95.5 % CHCl <sub>3</sub> (3)<br>1.0 % H <sub>2</sub> O  | 146                         |
| 2   | 56.0 % HA <sub>c</sub><br>13.3 % CHCl <sub>3</sub> (3)<br>30.7 % H <sub>2</sub> O | 2.9 % HA <sub>c</sub><br>96.0 % CHCl <sub>3</sub> (6)<br>1.1 % H <sub>2</sub> O  | 143                         |
| 3   | 83.9 % HA <sub>c</sub><br>5.1 % CHCl <sub>3</sub> (2)<br>11.0 % H <sub>2</sub> O  | 27.7 % HA <sub>c</sub><br>66.8 % CHCl <sub>3</sub> (4)<br>5.6 % H <sub>2</sub> O | 39                          |
| 4   | 65.7 % HA <sub>c</sub><br>4.8 % CHCl <sub>3</sub> (2)<br>29.6 % H <sub>2</sub> O  | 7.9 % HA <sub>c</sub><br>89.5 % CHCl <sub>3</sub> (3)<br>2.6 % H <sub>2</sub> O  | 74                          |
| 5   | 65.0 % HA <sub>c</sub><br>24.0 % CHCl <sub>3</sub> (3)<br>11.0 % H <sub>2</sub> O | 7.0 % HA <sub>c</sub><br>91.6 % CHCl <sub>3</sub> (3)<br>1.4 % H <sub>2</sub> O  | 106                         |

<sup>\*</sup> in mm Hg

LEGEND TO FIGURE 19

The Liquid Compositions for Which Data  
Are Obtained in Ternary System

- Total Pressures
- Vapour-Liquid Compositions

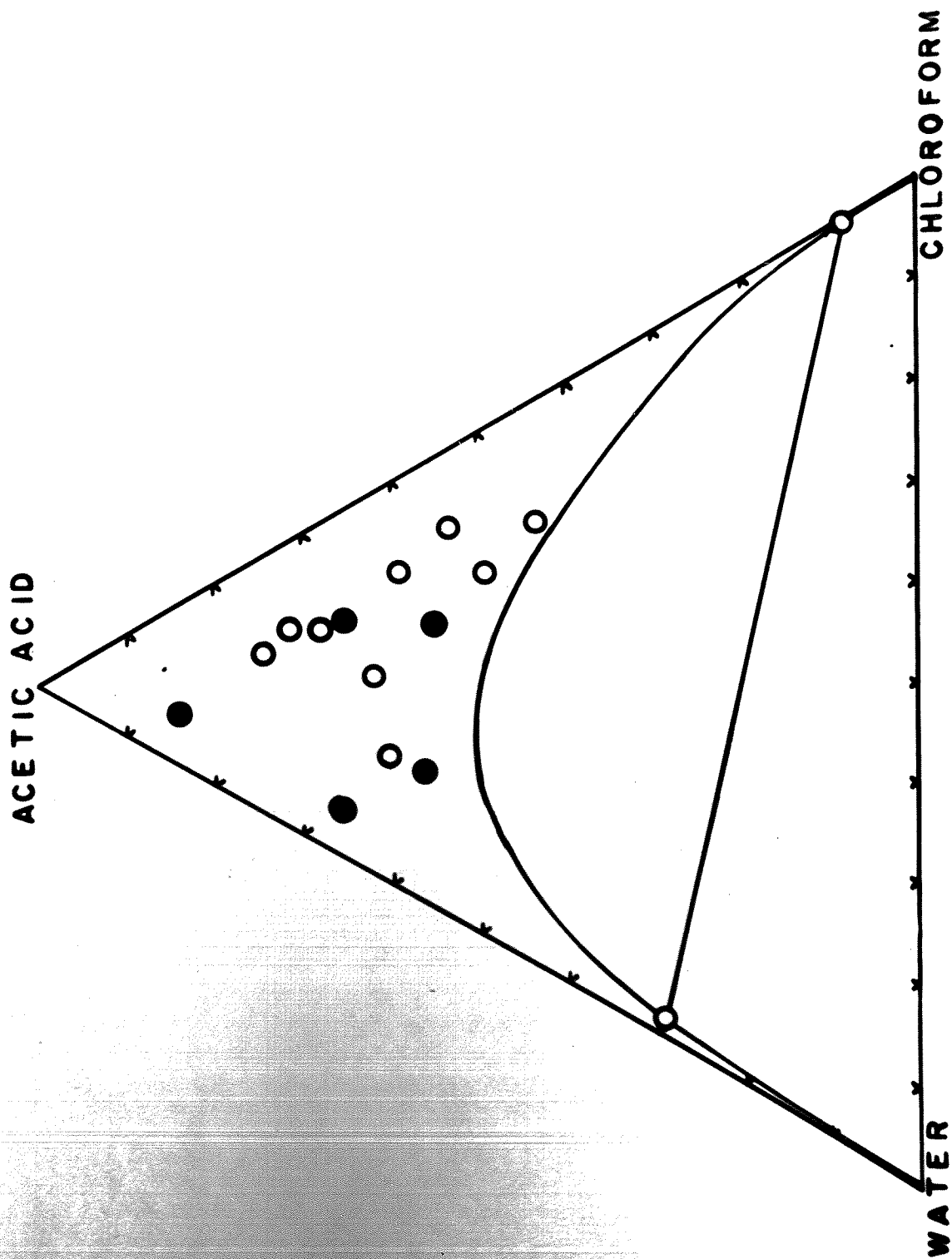


TABLE 21

DIMERIZATION DATA FOR THE SYSTEM  
ACETIC ACID-CHLOROFORM-WATER AT 25°C

| No. |                   | Liquid |        | Vapour |        | M     | %<br>dimer |
|-----|-------------------|--------|--------|--------|--------|-------|------------|
|     |                   | Wt. %  | Mole % | Wt. %  | Mole % |       |            |
| 1   | HA <sub>c</sub>   | 55.0   | 31.0   | 3.5    | 6.2    | 106.7 | 77.7       |
|     | CHCl <sub>3</sub> | 28.6   | 14.4   | 95.5   | 90.1   |       |            |
|     | H <sub>2</sub> O  | 16.4   | 54.6   | 1.0    | 3.7    |       |            |
| 2   | HA <sub>c</sub>   | 56.0   | 22.6   | 2.9    | 3.1    | 105.5 | 75.7       |
|     | CHCl <sub>3</sub> | 13.3   | 4.8    | 96.0   | 90.1   |       |            |
|     | H <sub>2</sub> O  | 30.7   | 72.6   | 1.1    | 6.8    |       |            |
| 3   | HA <sub>c</sub>   | 83.9   | 54.0   | 27.7   | 22.6   | 109.3 | 82.1       |
|     | CHCl <sub>3</sub> | 5.1    | 3.0    | 66.8   | 49.8   |       |            |
|     | H <sub>2</sub> O  | 11.0   | 43.0   | 5.6    | 27.7   |       |            |
| 4   | HA <sub>c</sub>   | 65.7   | 26.7   | 7.9    | 7.6    | 107.0 | 78.2       |
|     | CHCl <sub>3</sub> | 4.8    | 1.8    | 89.5   | 77.5   |       |            |
|     | H <sub>2</sub> O  | 29.6   | 71.5   | 2.6    | 14.9   |       |            |
| 5   | HA <sub>c</sub>   | 65.0   | 42.4   | 7.0    | 7.2    | 108.7 | 81.0       |
|     | CHCl <sub>3</sub> | 24.0   | 14.3   | 91.6   | 86.2   |       |            |
|     | H <sub>2</sub> O  | 11.0   | 43.3   | 1.4    | 6.6    |       |            |

Contd.

TABLE 21 CONTD.

| No. | $P_{total}^*$ | $P_{H_2O}$ | $P_{CHCl_3}$ | $P_{HA_c}$ | $P''$ | $P'$ | K   |
|-----|---------------|------------|--------------|------------|-------|------|-----|
| 1   | 146           | 9.1        | 131.5        | 5.4        | 4.2   | 1.2  | 2.9 |
| 2   | 143           | 9.7        | 128.8        | 4.4        | 3.3   | 1.1  | 2.9 |
| 3   | 39            | 10.8       | 19.4         | 8.8        | 7.2   | 2.5  | 2.9 |
| 4   | 74            | 11.0       | 57.3         | 5.6        | 4.4   | 1.2  | 2.9 |
| 5   | 106           | 6.9        | 91.4         | 7.7        | 6.2   | 1.5  | 2.9 |

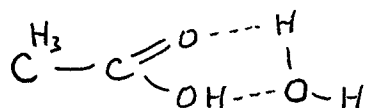
\* in mm Hg

Average K = 2.9

DISCUSSION OF THE RESULTS

A. THE SYSTEM WATER-ACETIC ACID

The system water-acetic acid shows contraction on mixing, resulting in a negative excess molar volume function as shown in Figure 4. The minimum negative value which is larger than 1 millilitre per mole of mixture occurs at a concentration of 50 mole percent. In general dipole-dipole mixtures show a similar behaviour, and this means that the dipole-dipole associations of the pure liquids are at least partially broken up to form mixed associations which cause the volume to decrease. I suggest that in the case of the system acetic acid-water a mixed association between one molecule acetic acid and one molecule water is formed, which association will be due to hydrogen bonding



The curves for the partial molal excess volumes as represented in Figure 5 seem to agree with this view, because there is a perfect symmetry in the behaviour of the two curves for water and for acetic acid. This symmetry also implies that the change in the liquid structure on addition of water to pure acetic acid and of acetic acid to pure water have similar effects with respect to the change in structure of the liquid. This

is for example quite contrary to the case of the system water-ethyl alcohol, where hydrogen bonding also is involved. This system has been described by Mitchel and Wynne-Jones<sup>44</sup> (1953).

In accordance with the previous remarks on the association it is interesting to note that the viscosities as reported by Campbell and Kartzmark<sup>31</sup> show also a perfect symmetry with a maximum at 50 mole percent acetic acid.

From the data on the molar refractions as reported in Table 6 it follows that the influence of the mixing process on the true volumes of acetic acid and water is very small. The deviations are positive, but as a first approximation additivity of the true volumes remains valid in a liquid mixture of acetic acid and water. This is confirmed by the constancy of the apparent molar refraction of the acetic acid.

Table 11 shows that the dimerization treatment is justified, because a constant value of the dimerization constant within the experimental error is obtained over the entire concentration region. The percentage dimerization decreases with the addition of water.

The results obtained with the partial pressures,



calculated on the basis of dimerization, in a treatment as suggested by von Zawidzki are very interesting.

Table 12 shows that the calculated results reproduce the measured values fairly well, which means that the Gibbs-Duhem-Margules equation (17) is satisfied.

A study of the Figures 9 and 11 shows that the system exhibits a positive deviation from Raoult's Law, in which case the excess free energy of mixing  $G^E$  will be greater than zero. No maximum was obtained in the vapour pressure curve. Figure 10 also suggests that there is no azeotropic point, at which the composition of the liquid and the coexisting vapour phase would be the same. It would therefore be possible to separate the two components completely by means of an isothermal fractional distillation.

A study of the graph for  $f(y)$  (see Figure 12) in relation to the theory as has been discussed on page 15 leads to the conclusion that the second derivative of the excess Gibbs free energy with respect to the concentration,  $\frac{d^2 G^E}{dx^2}$ , is equal to zero somewhere in the concentration region. This means that the  $G^E(x)$  curve will show a point of inflexion. The approximate location of both the maximum and the point of inflexion in

the  $G^E(x)$  curve are found from the curve in Figure 13. When 0.664  $\alpha$  becomes equal to unity, the corresponding concentrations are the concentrations belonging to the maximum and the point of inflexion. The two corresponding concentrations on a non-dimerized basis are 0.7 and 0.1 mole fraction of acetic acid in the liquid phase.

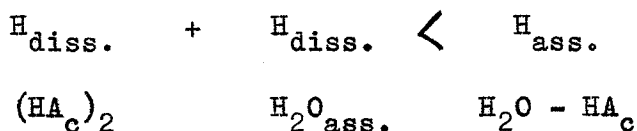
Because of the volume contraction the excess entropy of mixing will be negative. The relation between the excess entropy of mixing and the excess free energy of mixing is as follows:

$$G^E + T S^E = H$$

From this it follows that there are two possibilities for the sign of H, the heat of mixing. The International Critical Tables provide some heats of mixing at room temperature for several concentrations. Between 15 and 95 mole percent acetic acid a positive H is reported and for the other concentrations H is negative. Where H is positive the  $G^E$  term is larger than the  $TS^E$  term, and where  $H < 0$  the  $G^E$  term is lower than the  $TS^E$  term. This may very well explain the point of inflexion which occurs in the concentration range around 10 mole percent acetic acid.

In the case of volume contractions in dipole-dipole

liquids one expects usually a negative heat of mixing. The fact that positive heats result in the case of the system acetic acid-water can be explained according to the ideas put forward by Joerges and Nikuradse<sup>20</sup>. For the breaking up of the associations of water and acetic acid energy is required and by the new association between the water and the acetic acid energy is set free. The "dissociation" energies can be large. On page 17 it is reported that the energy of dimerization of acetic acid is  $-16\text{K cal/mole}$ , due to the fact that a double hydrogen bond is involved. This energy is certainly larger than that required to break up a water association. The number of mixed associations cannot be larger, and is usually smaller than the total of dissociations that take place. This means that even in the case where



a positive  $H$  of mixing can result. Thus, the energy required to break up the associations is larger than the energy set free by the formation of a mixed association.

It should be mentioned that the exact determination of the magnitude of  $G^E$  from the vapour pressure data is

not possible. This is because in the case of associations in the vapour phase extra terms in addition to those mentioned in equation (22) have to be used. These extra terms involve the second virial coefficients, which become more complicated in systems where associations occur in the vapour phase. This is shown by Lambert<sup>15</sup> in his paper on these vapour associations. No attempt has been made to find the correct procedure for the calculation of the excess free energy of mixing.

From a renewed study of the heats of mixing at 25°C, and a possible application of statistical thermodynamics a better understanding of the  $G^E$  function may be obtained. Scott<sup>45</sup> (1953) remarks that in the case of dispersion force solutions the theory of Prigogine and Mathot<sup>46</sup> (1952) gives a positive heat of mixing associated with a negative volume change and a negative excess entropy. Although this theory would not fit completely the observations in the system acetic acid-water an application of a similar theory may lead to valid results.

The data obtained indicate that the excess free energy function  $G^E$  is larger than zero, showing a point of inflexion. The heat of mixing  $H$  has both positive and negative values and shows a point of inflexion. The excess entropy of mixing function  $TS^E$  has a negative sign and possibly exhibits a point of inflexion.

With the aid of these data the system acetic acid-water at 25°C can be classified according to the rules proposed by Kamke<sup>6</sup>.

#### B. THE SYSTEM ACETIC ACID-CHLOROFORM

This system shows a dilation of the volume on mixing as is shown in the graphical representation of the excess molar volume in Figure 6. Although the system in question is a dipole-dipole mixture we do not get a negative excess volume. This indicates that there is a tendency to retain the identity of the original associations, rather than a tendency to form mixed associations between acetic acid and chloroform molecules. The maximum value of  $V^E$  occurs at a concentration of 45 mole percent chloroform. Moreover the excess partial molal volume curves do not show a symmetry as was the case in the system water-acetic acid.

The data for the molar refractions of the mixtures as reported in Table 7 show that the molar refractions are approximately additive. Hence the true molecular volumes remain practically unchanged during the process of mixing.

Table 16 shows again that the dimerization treatment is justified, because again there is a constancy of the

dimerization constant within the experimental error. The concentration dependence of the percentage dimerization of the acetic acid in the vapour phase follows the same pattern as in the system acetic acid-water. At first it was tempting to ascribe the decrease in the percentage dimerization of the acetic acid with the increasing concentration of water in the system acetic acid-water, to the formation of water-acetic acid associations, but the fact that in the system chloroform-acetic acid the percentage dimerization follows the same pattern, makes this conclusion improbable.

A treatment of the partial pressures, calculated on the dimerized basis, according to the method proposed by von Zawidzki shows that with a reasonable approximation the Gibbs-Duhem-Margules equation is satisfied, although for the case of the acetic acid the calculated values are somewhat on the low side.

From Figure 16 it follows that the behaviour of the system is practically ideal as far as Raoult's Law is concerned. There is a slight tendency to a positive deviation. If the pressure is plotted in dependence on the mole fraction on a non-dimerized basis the "deviation" from Raoult's Law is very distinct. A comparison of Figure 16 and Figure 14 seems to indicate that the linear

relationship, which the total pressure shows when plotted against the concentration in weight percentage is not coincidental. This seems a further justification for the dimerization treatment, in which the average molecular weight of the acetic acid becomes practically equal to that of the chloroform, and hence the weight fraction practically equal to the mole fraction.

From Figure 15 and Figure 16 it follows that by means of an isothermal fractional distillation the two components can be separated completely.

A study of Figure 17 and Figure 18 provides further evidence that the behaviour of the system is nearly ideal. In the ideal case the function  $0.079 \alpha$  will be equal to unity for all concentrations. The distribution of the points around the "ideal line" shows that the deviations from ideality may be due to experimental error.

According to the International Critical Tables the heat of mixing is positive, but only data for extreme dilution on both sides of the concentration region are available. Because the excess free energy function  $G^E$  is only slightly positive a negative excess entropy can be expected. Until a more detailed study of the heats of mixing is available a conclusion with respect to the sign of the excess entropy remains inadvisable. Because of this a

classification according to the rules proposed by Kamke is as yet impossible.

### C. THE SYSTEM ACETIC ACID-WATER-CHLOROFORM

Figure 8 exhibits a line running from pure acetic acid to pure chloroform where the excess volume  $V^E$  is equal to zero. This indicates that as far as the volume of the mixture is concerned there exists ideality. However, as will follow from the pressure data, this pseudo-ideality seems to be the result of the deviations from ideality, which are opposed to each other, in the three binary systems. The Figure also suggests that the excess volume in the system water-chloroform is negative for the complete region of concentration.

A study of the results as presented in Table 19 shows that in the ternary system large positive deviations from ideality occur. These large deviations are due to the presence of the water and the chloroform molecules, which show in the binary system a tendency to complete immiscibility. Also the total vapour pressure in this system is larger than that of the two pure components in the heterogeneous region, c.f. no. 11 in Table 19. This indicates a large positive value for the excess Gibbs free energy  $G^E$ . It can be seen that if the concentrations are expressed in



mole percentages only a small part of the concentration region is covered. For this reason it is difficult to show that for concentrations where the excess molar volume is equal to zero pseudo-ideality also exists for the vapour pressures. However, from the general behaviour of the vapour pressures such an ideality cannot be expected. Also the heats of mixing in the three binary systems suggest a positive value over the complete concentration region of the ternary system. This, however, has to be proved experimentally.

From the above discussion it can be concluded that the  $G^E$  function is positive for all concentrations. More information will be needed to decide on the behaviour of the heats of mixing and the entropies of mixing. A study of the dielectric properties of the system may very well throw some light on the last question. A classification on the basis of the functions  $G^E$ ,  $H$  and  $TS^E$  as proposed by Kamke and Kummerle is therefore as yet not possible until further evidence is obtained.

SUMMARY AND CONCLUSIONS

Studies have been made of the volume changes on mixing of two binary mixtures acetic acid-water and acetic-acid-chloroform, and of the ternary mixtures in the system acetic acid-chloroform-water. In the binary system acetic acid-water a volume contraction occurs, showing a minimum excess molar volume at 50 mole per cent. Partial molal volume studies suggest the formation of a mixed association between one molecule water and one molecule acetic acid. In the binary system acetic acid-chloroform the excess molar volume function is positive over the complete concentration range. From this a positive deviation from Raoult's Law is expected.

Studies of the refractive properties of the two binary systems show that the true molecular volumes of the acetic acid, water and chloroform are additive on mixing.

Studies of the vapour-liquid equilibria show that in all the three constituent binary systems a positive deviation from Raoult's Law exists. However, on the basis of the dimerization of acetic acid in the vapour phase it is found that the behaviour in the system acetic acid-chloroform is virtually ideal. The vapour pressures in the ternary system show a strong positive

deviation from Raoult's Law. It can be safely assumed that this positive deviation prevails over the complete concentration region. This proves that the line of pseudo-ideality, which runs through the composition triangle of the ternary system and which refers to the line of zero excess molar volume, does not represent the concentrations where "ideal behaviour" can be expected. These zero excess molar volumes are caused by the counteracting effects of water and chloroform molecules on acetic acid molecules.

In the two binary systems that were investigated it was found that the observed data satisfy the Gibbs-Duhem-Margules equation. This proves that a treatment for dimerization of the acetic acid in the vapour phase is permissible and indeed necessary.

Not enough evidence has as yet been collected for a complete classification of the three binary systems and the ternary systems according to the functions  $G^E$ ,  $H^E$  and  $TS^E$ .

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